

1. THEORY OF MOLECULAR MULTIPHOTON TRANSITIONS

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I. Introduction

In recent years, there has been a great advance in the visible and/or UV multiphoton spectroscopy to investigate mechanisms of higher order molecule-photon interactions, structure of vibronic states, and the dynamic behaviors taking place in the electronically excited states of molecules.¹⁻⁸

In this chapter, we are concerned with theoretical treatments of resonant molecular multiphoton transitions with emphasis on our work carried out during the past five years.

A multiphoton process is said to be in resonance if the energy of one or several quanta of photon is close to a transition energy between relevant two electronic states. In the resonant multiphoton transition, effects of dampings in the resonant states make a significant contribution to the multiphoton process. These effects originate from intramolecular interactions such as nonadiabatic, vibronic, rovibronic interactions, and/or from intermolecular interactions including inelastic and elastic interactions. One of the simplest method for derivation of an expression for the multiphoton transition probability in the resonant case is to use the expression derived in the non-resonant case by introducing the damping constants into the denominator of the cross section. The transition probability is expressed in the perturbation theory as⁹

$$W^{(n)} = \frac{\sigma^{(n)} I^n}{(\hbar\omega_R)^n} \quad (1.1)$$

where $\sigma^{(n)}$, I and ω_R denote the cross section for n -photon processes in units of $\text{cm}^{2n} \text{s}^{-n-1}$, the laser intensity in units of $\text{erg cm}^{-2} \text{s}^{-1}$, and the laser frequency, respectively. Equation (1.1) expresses simultaneous n -photon processes. Each energy denominator involved in $\sigma^{(n)}$ takes a real form which is expressed in terms of the laser frequency, and the frequency difference between relevant two levels. By using the treatment mentioned above, we can avoid divergence of the transition probability and calculate the magnitude of the transition probability for the simultaneous resonant multiphoton process. It is, however, insufficient to discuss the mechanism of resonant multiphoton transitions. In that treatment, for example, sequential multiphoton transitions can not be considered. In order to discuss the mechanism of the resonant multiphoton processes of molecules, it is necessary to properly take into account the damping effects. These effects have to be considered prior to take time $t \rightarrow \infty$ in deriving the transition probability expression in the perturbation theory.

In Sec. II, a theory of the resonant multiphoton transitions, based on the master equation approach is first presented to take into account the damping effects. An expression for the dephasing constant is derived. It is interesting to investigate the resonant multiphoton transition

and the resonant light scattering of molecules via coherently excited resonant states. The creation of the coherent states has been proved by observing quantum beats in fluorescence of molecules. A theoretical treatment about the time dependence of vibronic states after the coherent excitation is given in the density matrix formalism in Sec. II. Transition rates of two-photon transitions via the coherent excited resonant states are finally formulated in Sec. II.

In Sec. III, several applications of the theoretical treatment described in Sec. II are presented: Mechanisms of resonant two- and three-photon transitions, quantum beats in fluorescence, and time-resolved resonance Raman scattering from molecules with a nonequilibrium vibronic distribution are discussed.

II. General theory

II-1. Derivation of master equation

In this section, we derive the master equation which describes resonant multiphoton processes of molecules interacting with the heat bath. The master equation can be obtained by using the projection operator method,¹⁰⁻¹² or the cumulant expansion method.¹³⁻¹⁶ We adopt the projection operator method here.

We consider a total system consisting of molecules (denoted by S), the heat bath (B) and the radiation field (R). The wave functions of the total system $\psi_{\mathbf{i}}(t)$ satisfy the time-dependent Schrödinger equation:

$$i\hbar \frac{\partial}{\partial t} |\psi_{\mathbf{i}}(t)\rangle = \hat{H} |\psi_{\mathbf{i}}(t)\rangle . \quad (2.1)$$

Rather than describing the time-dependent behavior of the system in terms of the wave functions, it is convenient to use the density matrix defined by

$$\rho(t) = \sum_{\mathbf{i}} N_{\mathbf{i}} |\psi_{\mathbf{i}}(t)\rangle \langle \psi_{\mathbf{i}}(t)| , \quad (2.2)$$

where $N_{\mathbf{i}}$ represent the weighting factor. The density matrix can be expanded in terms of any basis set $\{|m\rangle\langle n|\}$ in the Liouville space (double space) as

$$\rho(t) = \sum_{\mathbf{m}} \sum_{\mathbf{n}} \rho_{\mathbf{mn}}(t) |m\rangle\langle n| , \quad (2.3)$$

and the vector in the Liouville space is defined as

$$|\rho(t)\rangle\rangle = \sum_{\mathbf{m}} \sum_{\mathbf{n}} \rho_{\mathbf{mn}}(t) |mn\rangle\rangle . \quad (2.3a)$$

The expansion coefficients $\rho_{\mathbf{mn}}(t)$ which is the projection of $\rho(t)$ on the basis vector $|mn\rangle\rangle$ in the Liouville space, are given by

$$\rho_{mn}(t) = \sum_i N_i C_{im}(t) C_{in}^*(t) , \quad (2.4)$$

which is obtained by applying the following expansion of the ordinary wave vector to Eq. (2.2)

$$|\psi_i(t)\rangle = \sum_m C_{im}(t) |m\rangle . \quad (2.5)$$

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

$$-\frac{\partial}{\partial t} \rho(t) = i\hat{L}\rho(t) , \quad (2.6)$$

where the Liouville operator \hat{L} is defined as

$$\hat{L} = [\hat{H}, \]/\hbar , \quad (2.7)$$

which can be derived by using Eqs. (2.1) and (2.2), and the Hamiltonian of the total system is given by

$$\hat{H} = \hat{H}_0 + \hat{H}'_{SR} + \hat{H}'_{SB} , \quad (2.8)$$

with
$$\hat{H}_0 = \hat{H}_S + \hat{H}_B + \hat{H}_R . \quad (2.9)$$

Here, \hat{H}_S , \hat{H}_B , and \hat{H}_R denote the Hamiltonians of the molecules, heat bath and photon field, respectively. \hat{H}'_{SR} and \hat{H}'_{SB} represent the interaction Hamiltonian between the molecule and photon field, and that between the molecule and heat bath, respectively. We have assumed that there is no interaction between the heat bath and photon field.

Applying the Laplace transformation

$$\rho(p) = \int_0^{\infty} dt \rho(t) e^{-pt} , \quad (2.10)$$

to Eq. (2.6), we obtain

$$(p+iL)\rho(p) = \rho(0) , \quad (2.11)$$

where $\rho(0)$ is the density matrix $\rho(t)$ at $t = 0$, and is assumed to be given by $\rho(0) = \rho^{(S)}(0)\rho^{(B)}(0)\rho^{(R)}(0)$, that is, the subsystems of the total system are independent each other at $t = 0$. It is assumed that these density matrices at $t = 0$ have zero off-diagonal matrix elements.

We are now in a position to find the equation of motion for the reduced density matrix of the molecules. This can be accomplished by applying two types of the projection operators to the density matrix equation of the total system. These are the projection operators which trace out the heat bath variables and photon field ones. In order to tracing out the heat bath variables, we define the projection operator

$$\hat{A} = \rho^{(B)}(0) \text{Tr}_B, \quad (2.12)$$

in which $\hat{A}^2 = \hat{A}$. Applying \hat{A} and $1-\hat{A}$ to Eq. (2.11) yields

$$\hat{A}[p+i\hat{L}]\hat{A}\rho(p) + \hat{A}[p+i\hat{L}](1-\hat{A})\hat{\rho}(p) = \hat{A}\rho(0), \quad (2.13)$$

and

$$(1-\hat{A})[p+i\hat{L}]\hat{A}\rho(p) + (1-\hat{A})[p+i\hat{L}](1-\hat{A})\rho(p) = 0, \quad (2.14)$$

respectively. Substituting $(1-\hat{A})\hat{\rho}(p)$ of Eq. (2.14) into Eq. (2.13), we obtain

$$A[p+i\hat{L}_0+i\hat{L}'_{SR}+\hat{\Sigma}(p)]\hat{A}\hat{\rho}(p) = \hat{A}\rho(0), \quad (2.15)$$

where

$$\hat{\Sigma}(p) = i\hat{L}'_{SB} + \hat{L}'_{SB}(1-\hat{A})[p+i\hat{L}]^{-1}(1-\hat{A})\hat{L}'_{SB}, \quad (2.16)$$

or

$$\hat{\Sigma}(p) = i\hat{L}'_{SB} - i\hat{L}'_{SB}(1-A)[p+i\hat{L}^0+i\hat{L}'_{SR}]^{-1}(1-\hat{A})\hat{\Sigma}(p), \quad (2.17)$$

and $\hat{L}^0 = [\hat{H}_0, \]/\hbar$ and $\hat{L}'_{SB} = [\hat{H}'_{SB}, \]/\hbar$. Equation (2.15) can be rewritten as

$$[p+i\hat{L}_{SR}^0+i\hat{L}'_{SR}+\langle\hat{\Sigma}(p)\rangle_B]\rho^{(SR)}(p) = \rho^{(SR)}(0) , \quad (2.18)$$

where

$$\hat{L}_{SR}^0 = [\hat{H}_S^0+\hat{H}_R^0, \quad]/\hbar ,$$

$$\rho^{(SR)}(p) = \text{Tr}_B \rho(p) , \quad (2.19)$$

and

$$\langle\hat{\Sigma}(p)\rangle_B = \text{Tr}_B \hat{\Sigma}(p) \rho^{(B)}(0) . \quad (2.20)$$

Neglecting the contribution of the molecule-photon field interaction in the self-energy operator of Eq. (2.17) and within the second Born approximation to the molecule-heat bath interaction, we can express Eq. (2.20) as

$$\langle\hat{\Sigma}(p)\rangle_B \simeq \text{Tr}_B \hat{L}'_{SB} [p+i\hat{L}^0]^{-1} \hat{L}_{SB} \rho^{(B)}(0) . \quad (2.21)$$

We next trace out the radiation field variables by applying the projection operator defined by

$$\alpha = \rho^{(R)}(0) \text{Tr}_R , \quad (2.22)$$

to Eq. (2.18) with Eq. (2.21). By using the same procedure described above, we obtain

$$[p+i\hat{L}_S^{+<<}] \langle (p) \rangle_B \langle (p) \rangle_R^{+<\pi} \sigma(p) = \sigma(0) , \quad (2.23)$$

where

$$\langle \dots \rangle_R = \text{Tr}_R \{ \dots \rho^{(R)}(0) \} ,$$

$$\sigma(p) = \text{Tr}_R \rho^{(SR)}(p) ,$$

and

$$\pi(p) = i\hat{L}_{SR}^! + \hat{L}_{SR}^! (1-\alpha) G_{SR}(p) (1-\alpha) \hat{L}_{SR}^! , \quad (2.24)$$

or

$$\pi(p) = i\hat{L}_{SR}^! - i\hat{L}_{SR}^! (1-\alpha) G_{SR}(p) (1-\alpha) \pi(p) , \quad (2.25)$$

with

$$G_{SR}(p) = [p+i\hat{L}_{SR}^0 + \langle (p) \rangle_B]^{-1} . \quad (2.26)$$

Using Eq. (2.25), we expand Eq. (2.23) as

$$[p+i\hat{L}_S^{+<\pi} \langle (0) \rangle_R \langle (1) \rangle_R \langle (2) \rangle_R \dots] \sigma(p) = \sigma(0) , \quad (2.27)$$

where $\langle \pi^{(n)} \rangle_R$ represent the transition operators for the n-photon processes in the P representation, and are given as

$$\pi^{(0)}(p) = \langle \hat{\Sigma}(p) \rangle_B, \quad (2.28)$$

$$\pi^{(1)}(p) = \hat{L}'_{SR} G_{SR}(p) \hat{L}'_{SR}, \quad (2.29)$$

$$\pi^{(2)}(p) = -\hat{L}'_{SR} G_{SR}(p) \hat{L}'_{SR} G_{SR}(p) \hat{L}'_{SR} G_{SR}(p) \hat{L}'_{SR}, \quad (2.30)$$

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Carrying out the inverse Laplace transformation of Eq. (2.27) yields

$$\begin{aligned} \frac{\partial}{\partial t} \sigma(t) = & -i \hat{L}'_S \sigma(t) - \int_0^t dy \langle \pi^{(0)}(y) \rangle_R \sigma(t-y) \\ & - \int_0^t dy [\langle \pi^{(1)}(y) \rangle_R + \langle \pi^{(2)}(y) \rangle_R + \dots] \sigma(t-y), \end{aligned} \quad (2.31)$$

where

$$\pi^{(n)}(y) = \frac{1}{2\pi i} \int_{-i\infty+c}^{i\infty+c} dp \pi^{(n)}(p) \exp(py), \quad (2.32)$$

and the convolution theorem has been used:

$$\frac{1}{2\pi i} \int_{-i\infty+c}^{i\infty+c} dp F(p) H(p) \exp(pt) = \int_0^t dy F(y) H(t-y), \quad (2.33)$$

where $F(y)$ and $F(p)$ satisfy Eq. (2.32). $H(p)$ and $H(t-y)$ are defined in an analogous way. By using the definition of displacement operator

$$\sigma(t-y) = \exp\left(-y\frac{\partial}{\partial t}\right)\sigma(t) , \quad (2.34)$$

we can express Eq. (2.31) as

$$\begin{aligned} \frac{\partial}{\partial t}\sigma(t) = & -\hat{L}_S\sigma(t) - \int_0^t dy \langle \pi^{(0)}(y) \rangle_R \exp\left(-y\frac{\partial}{\partial t}\right)\sigma(t) \\ & - \int_0^t dy [\langle \pi^{(1)}(y) \rangle_R + \langle \pi^{(2)}(y) \rangle_R + \dots] \exp\left(-y\frac{\partial}{\partial t}\right)\sigma(t) . \end{aligned} \quad (2.35)$$

Equation (2.31) or (2.35) has a non-Markoffian structure. In other words, in order to determine the reduced density matrix $\rho(t)$ at $t = t_1$, we have to know time-dependence of the density matrix in the whole time range from the past ($t = 0$) to the present time ($t = t_1$).

In our treatment, we restrict ourselves to the Markoff processes. In this case, we obtain

$$\frac{\partial \sigma(t)}{\partial t} = -i\hat{L}_S\sigma(t) - \Gamma(t)\sigma(t) - W^{(1)}(t)\sigma(t) - W^{(2)}(t)\sigma(t) \dots, \quad (2.36)$$

where $W^{(n)}(t)$ represent the transition operators for the n -photon processes, $\Gamma(t) = W^{(0)}(t)$ with $n = 0$ and they are given by

$$W^{(n)}(t) = \int_0^t dy \langle \pi^{(n)}(y) \rangle_R \exp[it\hat{L}_S] . \quad (2.37)$$

We note that the population of the molecular eigenstate m at time t , $\sigma_{mm}(t)$ is defined in the Liouville space (see Eq. (2.3)) by $\langle\langle mm|\sigma(t)\rangle\rangle$. After projecting out the diagonal part of the both sides of Eq. (2.36) and taking time limit $t \rightarrow \infty$ in the transition operators, we obtain the kinetic equation (called master equation) for the population change related to the resonant multiphoton transitions:

$$\frac{d\sigma_{mm}(t)}{dt} = \sum_{a \neq m} (k_{ma}^{(0)} + k_{ma}^{(1)} + \dots) \sigma_{aa}(t) - (k_{mm}^{(0)} + k_{mm}^{(1)} + \dots) \sigma_{mm}(t) , \quad (2.38)$$

where $k_{ma}^{(n)}$, representing the n -photon transition rate constant from a to m molecular states, is given by

$$k_{ma}^{(n)} = \lim_{t \rightarrow \infty} W_{ma}^{(n)}(t) , \quad (2.39a)$$

with

$$W_{ma}^{(n)}(t) = -\langle\langle mm|W^{(n)}(t)|aa\rangle\rangle , \quad (2.39b)$$

and $k_{mm}^{(n)}$ represents the n -photon induced population decay constant of the state m , and is given in an analogous form as Eqs. (2.39). The rate equation approach based on Eq. (2.38) has been adopted in studying dynamics of molecules in the presence of the photon field such as UV and/or visible

multiphoton ionization dissociation reactions, and vibrational relaxations in the resonant states.⁹

II-2. The dephasing constant

In this section, an expression for the dephasing constant which makes an important contribution to the resonant multiphoton processes is presented, and the time evolution of the reduced density matrix after the coherence between the molecular eigenstates in the resonant state is created by irradiation of laser is considered within the isolated line approximation .

The equation of motion of the off-diagonal reduced density matrix element between m and n molecular eigenstates, $\sigma_{mn}(t) = \langle\langle mn|\sigma(t)\rangle\rangle$ in the absence of the photon field is given from Eq. (2.36) as

$$\frac{d}{dt}\langle\langle mn|\sigma(t)\rangle\rangle = \sum_{\mathbf{k}} \sum_{\ell} \langle\langle mn|\{\hat{i}L_S - \Gamma(t)\}|\mathbf{k}\ell\rangle\rangle \langle\langle \mathbf{k}\ell|\sigma(t)\rangle\rangle . \quad (2.40)$$

Real and imaginary parts of the diagonal matrix element of $\Gamma(t)$ in the Liouville space, for example, $\langle\langle mn|\Gamma(t)|mn\rangle\rangle$ ($\equiv \Gamma_{mn:mn}$) represent the time-dependent level shift and the dephasing rate between m and n states, respectively. The off-diagonal matrix element in the Liouville space, $\Gamma_{mn:\mathbf{k}\ell}$ represents the contribution of overlap between two transitions,

$k \neq \ell$ and $n \neq m$.

The off-diagonal matrix element $\Gamma_{mn:k\ell}$ is given by

$$\Gamma_{mn:k\ell}(t) = \int_0^t dy \langle \langle mn | \langle \langle \pi^{(0)}(y) \rangle_B \rangle_R | k\ell \rangle \rangle, \quad (2.41)$$

where

$$\begin{aligned} \langle \langle mn | \langle \langle \pi^{(0)}(y) \rangle_B \rangle_R | k\ell \rangle \rangle &= \text{Tr}_B \{ \langle \langle mn | \hat{L}'_{SB}(y) \exp[-iy\hat{L}_S] \hat{L}'_{SB} | k\ell \rangle \rangle \\ &\times \langle \langle k\ell | \exp[iy\hat{L}_S] | k\ell \rangle \rangle_{\rho^{(B)}}(0) \}, \end{aligned} \quad (2.42)$$

in which

$$\hat{L}'_{SB}(y) = \exp[iy\hat{L}_B] \hat{L}'_{SB} \exp[-iy\hat{L}_B]. \quad (2.43)$$

In reducing Eq. (2.42), the following relation between the matrix elements of the Liouville operator, \hat{L} and those of the Hamiltonian, \hat{H} , has been used:¹⁷

$$\begin{aligned} \langle \langle mn | \hat{L} | k\ell \rangle \rangle_{\hat{F}} &= \frac{1}{\hbar} (H_{mk} \delta_{n\ell} \hat{F} - \hat{F} H_{\ell n} \delta_{km}) \\ &= \frac{1}{\hbar} (H_{mk} \delta_{n\ell} - H_{\ell n}^{\times} \delta_{km}) \hat{F}, \end{aligned} \quad (2.44)$$

in which \hat{F} is an operator of a system coupled to the molecule, for example, the density matrix of the heat bath in the equilibrium for $\hat{H} = \hat{H}'_{SB}$. Subscript \times of H indicates that H^{\times} should be replaced with F . Equation (2.42) can be expressed as

$$\begin{aligned}
\langle\langle mn | \langle\langle \pi^{(0)}(y) \rangle_B \rangle_R | k \ell \rangle\rangle &= \frac{1}{\hbar^2} \sum_p \{ \exp[-iy\omega_{pk}] \langle V_{mp}(y) V_{pk} \rangle_B \delta_{n\ell} \\
&+ \exp[-iy\omega_{lp}] \langle V_{lp} V_{pn}(y) \rangle_B \delta_{mk} \} \\
&- \frac{1}{\hbar^2} \{ \exp[-iy\omega_{ln}] \langle V_{ln} V_{mk}(y) \rangle_B + \exp[-iy\omega_{mk}] \langle V_{ln}(y) V_{mk} \rangle_B \},
\end{aligned} \tag{2.45}$$

where ω_{mk} is the frequency difference between m and k levels, and

$$V_{mp}(y) = \langle m | \exp[iy\hat{H}_B/\hbar] \hat{H}'_{SB} \exp[-iy\hat{H}_B/\hbar] | p \rangle. \tag{2.46}$$

The diagonal matrix element of Eq. (2.42) can be written as

$$\begin{aligned}
\langle\langle mn | \langle\langle \pi^{(0)}(y) \rangle_B \rangle_R | mn \rangle\rangle &= \frac{1}{\hbar^2} \sum_{p \neq m} \{ \exp[-iy\omega_{pm}] \langle V_{mp}(y) V_{pm} \rangle_B \\
&+ \exp[-iy\omega_{np}] \langle V_{np} V_{pn}(y) \rangle_B \} + \frac{1}{\hbar^2} \langle V_{mm}(y) V_{mm} \rangle_B \\
&+ \frac{1}{\hbar^2} \langle V_{nn} V_{nn}(y) \rangle_B - \frac{1}{\hbar^2} \langle V_{nn} V_{mm}(y) \rangle_B - \frac{1}{\hbar^2} \langle V_{nn}(y) V_{mm} \rangle_B.
\end{aligned} \tag{2.47}$$

The first two terms and the others in Eq. (2.47) originate from the dephasing effects due to inelastic and elastic molecule-heat bath interactions, respectively.

When the molecule is excited within its resonance width of the molecular eigenstate, we can take t as $t \rightarrow \infty$ in calculating the matrix element of $\Gamma(t)$. This is called the

Markoff approximation. In the Markoff approximation, the dephasing constant related to m and n levels, $\Gamma_{mn:mn}$, for example is given by¹⁸

$$\Gamma_{mn:mn} = \frac{1}{2}(\Gamma_{mm:mm} + \Gamma_{nn:nn}) + \Gamma_{mn:mn}^{(d)} \quad , \quad (2.48)$$

where $\Gamma_{mm:mm}$ ($= k_{mm}^{(0)}$), and $\Gamma_{mn:mn}^{(d)}$ denote the population decay constant of the level m , and the pure dephasing constant resulting from the elastic interactions between the molecule and the heat bath, respectively, and they are expressed as

$$\Gamma_{mm:mm} = \frac{2\pi}{\hbar^2} \sum_j \sum_{\underline{j}} \sum_{\underline{m}} \rho_{\underline{mm}}^{(B)}(0) |(\hat{H}'_{SB})_{j\underline{j}, \underline{m}\underline{m}}|^2 \delta(\omega_{mj} - \omega_{\underline{j}\underline{m}}) \quad , \quad (2.49)$$

and

$$\Gamma_{mn:mn}^{(d)} = \frac{2\pi}{\hbar^2} \sum_{\underline{j}} \sum_{\underline{m}} \rho_{\underline{mm}}^{(B)}(0) |(\hat{H}'_{SB})_{\underline{m}\underline{j}, \underline{m}\underline{m}} - (\hat{H}'_{SB})_{\underline{n}\underline{j}, \underline{n}\underline{m}}|^2 \delta(\omega_{\underline{m}\underline{j}}) \quad , \quad (2.50)$$

where \underline{m} and \underline{j} indicate the initial and final levels of the perturber of the heat bath, respectively.

In the case in which two transitions, $m \leftarrow n$ and $k \leftarrow \ell$ do not overlap each other, we can neglect $\langle\langle mn | \Gamma(t) | k\ell \rangle\rangle$ for $|mn\rangle\rangle \neq |k\ell\rangle\rangle$ in the equation of motion of the reduced density matrix element, Eq. (2.40). This is called the isolated line approximation. In the isolated line approximation, the solution of Eq. (2.40) is given by

$$\langle\langle mn|\sigma(t)\rangle\rangle = \langle\langle mn|G_S(t)|mn\rangle\rangle\langle\langle mn|\sigma(0)\rangle\rangle, \quad (2.51)$$

or

$$\langle\langle mn|\sigma(t)\rangle\rangle = \langle\langle mn|G_S(t-t_1)|mn\rangle\rangle\langle\langle mn|\sigma(t_1)\rangle\rangle, \quad (2.52)$$

where $G_S(t-t_1)$, the time evolution operator of the reduced density matrix, takes the form

$$G_S(t-t_1) = \exp\left[-\int_{t_1}^t dy\{i\hat{L}_S + \Gamma(y)\}\right]. \quad (2.53)$$

The matrix element of Eq. (2.53) is expressed as

$$\langle\langle mn|G_S(t-t_1)|mn\rangle\rangle = \exp\left[-i(t-t_1)\omega_{mn} - \int_{t_1}^t dy\Gamma_{mn:mn}(y)\right]. \quad (2.54)$$

In the Markoff approximation, Eq. (2.54) reduces to

$$\langle\langle mn|G_S(t-t_1)|mn\rangle\rangle = \exp[-(t-t_1)(i\omega_{mn} + \Gamma_{mn:mn})]. \quad (2.55)$$

where the real part of the dephasing constant has been omitted. Equation (2.52) with Eq. (2.54) or (2.55) represents the time evolution of the off-diagonal density matrix of the m and n states, created by a coherent laser pulse at $t = t_1$, and that the damping is dominated by the dephasing rate (constant).

II-3. Coherence between molecular eigenstates

In this section, the time evolution of molecules produced by a coherent excitation will be treated in terms of the reduced density matrix formalism. Appearance of quantum beats in fluorescence of molecules are directly related to the time dependence of the off-diagonal density matrix elements.¹⁷

Let us first specify the molecule-photon interaction Hamiltonian, H'_{SR} . In the dipole and rotating wave approximations the interaction Hamiltonian is given by

$$\hat{H}'_{SR} = -\sum_m \sum_n (M_{nm}(1)E^{(+)} |n\rangle\langle m| + \text{h.c.}) , \quad (2.56)$$

where $M_{nm}(1)$ is defined in terms of the dipole matrix element between the molecular states, m and n , M_{nm} and the polarization of photon e_1 as $M_{nm}(1) = M_{nm} \cdot e_1$, and $E^{(+)}$ is the electric field operator of the photon field and is expressed as

$$E^{(+)} = -i \left(\frac{\hbar}{2\epsilon_0 V} \right) \frac{1}{2} \sum_{\lambda} \omega_{\lambda} \frac{1}{\lambda} \hat{b}_{\lambda}^{+} , \quad (2.57)$$

in which V and \hat{b}_{λ}^{+} denote the volume of the photon field and the photon creation operator of mode λ with frequency ω_{λ} , respectively.

The equation of motion for the density matrix related to the one-photon absorption processes is given by Eq. (2.38)

with $n = 1$:

$$\frac{\partial}{\partial t} \sigma(t) = -\{i\hat{L}_S + \Gamma(t)\} \sigma(t) - \int_0^t dt_1 \langle \pi^{(1)}(y) \rangle_R \exp[it\hat{L}_S] \sigma(t) . \quad (2.58)$$

By using the perturbation method, we can obtain the solution as

$$\begin{aligned} \sigma(t) = & \exp\left[-\int_0^t dt_1 \{i\hat{L}_S + \Gamma(t)\}\right] \sigma(0) \\ & - \int_0^t dt_1 \int_0^{t_1} dt_2 G_S(t-t_1) \langle \hat{L}_{SR}(t_1-t_2) G_S(t-t_1) \hat{L}_{SR} \rangle_R \\ & \times \exp[i(t_1-t_2)\hat{L}_S] \sigma(0) . \end{aligned} \quad (2.59)$$

We consider the time evolution of the off-diagonal reduced density matrix $\sigma_{mn}(t)$ in which molecular eigenstates (m and n) are coherently excited from the initial state a . The off-diagonal matrix element $\sigma_{mn}(t) = \langle\langle mn | \sigma(t) \rangle\rangle$ can be written as

$$\begin{aligned} \langle\langle mn | \sigma(t) \rangle\rangle = & - \int_0^t dt_1 \int_0^{t_1} dt_2 \sum_k \sum_\ell \langle\langle mn | G_S(t-t_1) | mn \rangle\rangle \\ & \times \text{Tr}_R \{ \langle\langle mn | \hat{L}'_{SR}(t_1-t_2) | k\ell \rangle\rangle \langle\langle k\ell | G_S(t-t_1) | k\ell \rangle\rangle \\ & \times \langle\langle k\ell | \hat{L}'_{SR} | aa \rangle\rangle_{\rho}^{(R)}(0) \} . \end{aligned} \quad (2.60)$$

After the calculation of the matrix elements involving the Liouville operator \hat{L}'_{SR} by using Eq. (2.44), we can express

Eq. (2.60) as

$$\begin{aligned}
 \sigma_{mn}(t) = & \frac{M_{an}(1)M_{ma}(1)}{\hbar^2} \int_0^t dt_1 \int_0^{t_1} dt_2 [\langle E^{(+)}(t_1) E^{(-)}(t_2) \rangle_R \\
 & \times \langle \langle mn | G_S(t-t_1) | mn \rangle \rangle \langle \langle ma | G_S(t_1-t_2) | ma \rangle \rangle \\
 & + \langle E^{(+)}(t_2) E^{(-)}(t_1) \rangle_R \langle \langle mn | G_S(t-t_1) | mn \rangle \rangle \\
 & \times \langle \langle an | G(t_1-t_2) | an \rangle \rangle] , \tag{2.61}
 \end{aligned}$$

where $\langle \rangle_R$ represents the photon field correlation function.

The time dependence of the density matrix element related to the one-photon absorption processes can be described in terms of the diagrammatic representation shown in Fig. 2.1. The diagram in the left-hand side and that in the right-hand side correspond to the first and second terms in Eq. (2.61), respectively. The lower and upper lines represent the time evolution of the ket $| \rangle$ and bra $\langle |$ vectors of the molecule, respectively. Time develops from the left-to right-hand sides. The wavy line represents the molecule-photon interaction duration. The dotted points indicate the interaction points. The diagram in the left-hand side shows that the molecular coherence between the initial state a and the resonant state m is created and decays during the molecule-photon interaction time, t_1-t_2 . Following the photon absorption by the molecules, the molecular coherence between two excited states, m and n

begins to decrease because of the existence of dephasing processes. The time dependence is expressed by $\langle\langle mn | G_S(t-t_1) | mn \rangle\rangle$ which is given by Eq. (2.54) or Eq. (2.55) in the Markoff approximation.

So far we did not mention the definition of coherence. The degree of the coherence between the molecular eigenstates, m and n , $C(m,n)$ is given in terms of the reduced density matrices as¹⁷

$$C(m,n) = \left[\frac{\sigma_{mn}(t)\sigma_{nm}(t)}{\sigma_{mm}(t)\sigma_{nn}(t)} \right]^{\frac{1}{2}} \quad (2.62)$$

From the definition of density matrix, the degree of the coherence is smaller than or equal to one. $C(m,n)$ nearly equal to one means that the molecular state which is represented in terms of a linear combination of the m and n states is formed, in other words, the coherence is created between m and n states.

An application of the theory developed in this section to the quantum beats in fluorescence is given in Sec. III-2.

II-4. Two-photon transitions via coherently excited resonant states

Expressions for the two-photon transition rates are derived by using the transition operator derived in Sec. II-1. We focus our attention on the two-photon transition via coherently excited resonant states. It is interesting to investigate possibility of observing the interference effects between molecular eigenstates of the resonant states such as a non-Lorentzian band shape in the two-photon ionization spectra or quantum beats in the time-resolved spectra.

The two-photon transition rate from initial state a to the final state f via resonant intermediate states, $W_{fa}^{(2)}(t)$ is given from Eq. (2.37) as

$$W_{fa}^{(2)}(t) = -\langle\langle ff | W^{(2)}(t) | aa \rangle\rangle$$

$$= \int_0^t dt_1 \text{Tr}_R \{ \langle\langle ff | \pi^{(2)}(t-t_1) | aa \rangle\rangle \rho^{(R)}(0) \} , \quad (2.63)$$

in which two-photon transition operator, $\pi^{(2)}$ can be expressed as

$$\pi^{(2)}(t-t_1) = \frac{1}{2\pi i} \int_{-i\omega+c}^{i\omega+c} dp \{ -\hat{L}'_{SR} G_{SR}(p) \hat{L}'_{SR} G_{SR}(p) \hat{L}'_{SR} G_{SR}(p) \hat{L}'_{SR} \}$$

$$\times \exp[p(t-t_1)] . \quad (2.64)$$

By applying the convolution theorem to Eq. (2.64), substituting the resulting expression into Eq. (2.63) and changing the integration variables, we obtain

$$W_{fa}^{(2)}(t) = \left(\int_0^t dt_i \right) \text{Tr}_R \{ \langle\langle ff | \hat{L}'_{SR}(t_1) G_S(t_1-t_2) \hat{L}'_{SR}(t_2) \\ \times G_S(t_2-t_3) \hat{L}'_{SR}(t_3) G_S(t_3) \hat{L}'_{SR}{}^{(R)}(0) | aa \rangle\rangle \} , \quad (2.65)$$

where

$$\left(\int_0^t dt_i \right) = \int_0^t dt_1 \int_0^{t_1} dt_2 \int_0^{t_2} dt_3 .$$

$\langle\langle ff | \dots | aa \rangle\rangle$ in Eq. (2.65) consists of three types of the sequence (product) of the matrix elements of the Liouville operator \hat{L}'_{SR} :

$$\begin{array}{l} \hat{L}'_{SR} \quad \hat{L}'_{SR} \quad \hat{L}'_{SR} \quad \hat{L}'_{SR} \\ \text{A) } \quad aa \longrightarrow ma \longrightarrow fa \longrightarrow fm' \longrightarrow ff , \\ \text{B) } \quad aa \longrightarrow ma \longrightarrow mm' \longrightarrow fm' \longrightarrow ff , \\ \text{and} \\ \text{C) } \quad aa \longrightarrow ma \longrightarrow mm' \longrightarrow fm' \longrightarrow ff . \end{array} \quad (2.66)$$

Here three types of the sequence are denoted by A, B and C respectively. The sequences conjugate to Eq. (2.66) are

denoted by A^\dagger , B^\dagger and C^\dagger , respectively.

The two-photon transition rate consists of three types of the partial transition rate originating from $A(A^\dagger)$, $B(B^\dagger)$, and $C(C^\dagger)$ sequences, which are respectively indicated by $W^{(2A)}(t)$, $W^{(2B)}(t)$ and $W^{(2C)}(t)$:

$$W_{fa}^{(2)}(t) = 2\text{Re}\{W^{(2A)}(t) + W^{(2B)}(t) + W^{(2C)}(t)\} . \quad (2.67)$$

Each partial transition rate is defined as

$$\begin{aligned} W^{(2A)}(t) = & \left(\int_0^t dt_i \right) \sum_m \sum_{m'} \text{Tr}_R \{ \langle \langle ff | \hat{L}'_{SR}(t_1) | fm' \rangle \rangle \\ & \times \langle \langle fm' | G_S(t_1-t_2) | fm' \rangle \rangle \langle \langle fm' | \hat{L}'_{SR}(t_2) | fa \rangle \rangle \\ & \times \langle \langle fa | G_S(t_2-t_3) | fa \rangle \rangle \langle \langle fa | \hat{L}'_{SR}(t_3) | ma \rangle \rangle \\ & \times \langle \langle ma | G_S(t_3) | ma \rangle \rangle \langle \langle ma | \hat{L}'_{SR} | aa \rangle \rangle \rho^{(R)}(0) \} , \quad (2.68a) \end{aligned}$$

$$\begin{aligned} W^{(2B)}(t) = & \left(\int_0^t dt_i \right) \sum_m \sum_{m'} \text{Tr}_R \{ \langle \langle ff | \hat{L}'_{SR}(t_1) | fm' \rangle \rangle \\ & \times \langle \langle fm' | G_S(t_1-t_2) | fm' \rangle \rangle \langle \langle fm' | \hat{L}'_{SR}(t_2) | mm' \rangle \rangle \\ & \times \langle \langle mm' | G_S(t_2-t_3) | mm' \rangle \rangle \langle \langle mm' | \hat{L}'_{SR}(t_3) | ma \rangle \rangle \\ & \times \langle \langle ma | G_{SR}(t_3) | ma \rangle \rangle \langle \langle ma | \hat{L}'_{SR} | aa \rangle \rangle \rho^{(R)}(0) \} , \quad (2.68b) \end{aligned}$$

and

$$\begin{aligned}
W^{(2C)}(t) &= \left(\int_0^t dt_1 \right) \sum_{m m'} \text{Tr}_R \{ \langle \langle f f | \hat{L}'_{SR}(t_1) | m f \rangle \rangle \\
&\times \langle \langle m f | G_S(t_1 - t_2) | m f \rangle \rangle \langle \langle m f | \hat{L}'_{SR}(t_2) | m m' \rangle \rangle \\
&\times \langle \langle m m' | G_S(t_2 - t_3) | m m' \rangle \rangle \langle \langle m m' | \hat{L}'_{SR}(t_3) | m a \rangle \rangle \\
&\times \langle \langle m a | G_S(t_3) | m a \rangle \rangle \langle \langle m a | \hat{L}'_{SR} | a a \rangle \rangle \rho^{(R)}(0) \} . \quad (2.68c)
\end{aligned}$$

We consider a two-photon transition induced by different two photon fields E_1 and E_2 . In this case, after averaging over the photon field variables in Eqs. (2.68), we obtain

$$\begin{aligned}
W^{(2A)}(t) &= \sum_{m m'} \left(\int_0^t dt_1 \right) \langle E_1^{(+)}(t_2) E_1^{(-)}(0) \rangle_R \langle E_2^{(+)}(t_2) E_2^{(-)}(t_3) \rangle_R \\
&\times M_{am'}(1) M_{m'f}(2) M_{fm}(2) M_{ma}(1) \langle \langle f m' | G_S(t_1 - t_2) | f m' \rangle \rangle \\
&\times \langle \langle f a | G_S(t_2 - t_3) | f a \rangle \rangle \langle \langle m a | G_S(t_3) | m a \rangle \rangle , \quad (2.69a)
\end{aligned}$$

$$\begin{aligned}
W^{(2B)}(t) &= \sum_{m m'} \left(\int_0^t dt_1 \right) \langle E_1^{(+)}(t_3) E_1^{(-)}(0) \rangle_R \langle E_2^{(+)}(t_1) E_2^{(-)}(t_2) \rangle_R \\
&\times M_{am'}(1) M_{m'f}(2) M_{fm}(2) M_{ma}(1) \langle \langle f m' | G_S(t_1 - t_2) | f m' \rangle \rangle \\
&\times \langle \langle m m' | G_S(t_2 - t_3) | m m' \rangle \rangle \langle \langle m a | G_S(t_3) | m a \rangle \rangle , \quad (2.69b)
\end{aligned}$$

and

$$\begin{aligned}
W^{(2C)}(t) &= \sum_m \sum_{m'} \int_0^t dt_i \langle E_1^{(+)}(t_3) E_1^{(-)}(0) \rangle_R \langle E_2^{(+)}(t_1) E_2^{(-)}(t_2) \rangle_R \\
&\times M_{am'}(1) M_{m'f}(2) M_{fm}(2) M_{ma}(1) \langle\langle mf | G_S(t_1-t_2) | mf \rangle\rangle \\
&\times \langle\langle mm' | G_S(t_2-t_3) | mm' \rangle\rangle \langle\langle ma | G_S(t_3) | ma \rangle\rangle . \quad (2.69c)
\end{aligned}$$

A diagrammatic representation of the time evolution of the ket and bra vectors in two-photon transitions is shown in Figs. 2.2. Figures 2.2a, 2.2b and 2.2c correspond to the time evolution in Eqs. (2.69a), 2.69b and 2.69c, respectively. In the case of $m = m'$, that is, neglecting the coherent effects, these diagrams, for example, reduce to those for the resonant light scattering problems investigated by Takagahara et al,^{19,20} and by Hanamura and Takagahara.²¹

So far, we have restricted ourselves to the two-photon transition. The rate of three-photon transitions can be taken into account in the similar way.

III. Application

III-1. Mechanisms of resonant multiphoton transitions

Terms "simultaneous process" and "sequential process" are frequently used in describing the multiphoton processes.^{8,9} For the nonresonant case, the simultaneous process in general makes the dominant contribution. On the other hand, for

the resonant case, the two mechanisms seem to operate on the multiphoton transition at the same time. The sequential transition is induced by two types of perturbations in the presence of laser light. One is inelastic perturbation such as intramolecular nonadiabatic interaction, or intermolecular interaction, which bring about electronic, vibrational and/or rotational relaxations. The other is an elastic interaction which causes so-called pure dephasing.

In this section, we first discuss the mechanism of a resonant two-photon transition by using the rate equation approach in which vibrational relaxations in the resonant states and the elastic interaction are taken into account. The structure of the two-photon transition probability $k_{fa}^{(2)}$ is analyzed on the basis of the formalism developed in Sec. II. The sequential transition induced by the pure dephasing process is derived. A difference in the vibronic intensity distribution between sequential and simultaneous processes is presented. Dephasing effects in three-photon absorptions are finally considered.

III-1A. Effects of vibrational relaxations for a resonant two-photon transition

We consider a model for a resonant two-photon transition shown in Fig. 3.1. Saturation effects are neglected for simplicity. By using Eq. (2.38), we can express the kinetic equations as²²

$$\frac{d\sigma_{aa}(t)}{dt} = -k_{aa}\sigma_{aa}(t) , \quad (3.1)$$

$$\begin{aligned} \frac{d\sigma_{mm}(t)}{dt} = & \sum_a k_{ma}^{(1)} \sigma_{aa}(t) - k_{mm} \sigma_{mm}(t) - \sum_{m'} k_{m'm}^{(0)} \sigma_{m'm}(t) \\ & + \sum_{m'} k_{mm'}^{(0)} \sigma_{m'm'}(t) , \end{aligned} \quad (3.2)$$

and

$$\frac{d\sigma_{ff}(t)}{dt} = \sum_a k_{fa}^{(2)} \sigma_{aa}(t) + \sum_m k_{fm}^{(1)} \sigma_{mm}(t) , \quad (3.3)$$

where $k_{aa} = k_{aa}^{(1)} + k_{aa}^{(2)}$, and $k_{mm} = \sum_n k_{nm}^{(1)}$. Defining the matrix elements of R as

$$R_{mm'} = \delta_{mm'} \sum_\ell k_{\ell m'}^{(0)} (1 - \delta_{\ell m}) - k_{mm'}^{(0)} (1 - \delta_{mm'}) , \quad (3.4)$$

we can rewrite Eq. (3.2) as

$$\frac{d\sigma_{mm}(t)}{dt} = \sum_a k_{ma}^{(1)} \sigma_{aa}(t) - k_{mm} \sigma_{mm}(t) - \sum_{m'} R_{mm'} \sigma_{m'm'}(t) . \quad (3.5)$$

Symmetrizing the relaxation matrix R by setting $\sigma_{mm}(t) = \tilde{\sigma}_{mm}(t) f_m^{1/2}$, in which f_m denotes the equilibrium vibrational distribution in the resonant state, we obtain the kinetic equation for $\tilde{\sigma}_{mm}(t)$ in the matrix formalism as

$$\frac{d\tilde{\sigma}(t)}{dt} = \tilde{C}(t) - (K+\tilde{R})\tilde{\sigma}(t) , \quad (3.5)$$

where $\tilde{C}_m(t) = \sum_a \tilde{k}_{ma}^{(1)} \sigma_{aa}(t)$ with $\tilde{k}_{ma}^{(1)} = k_{ma}^{(1)} f_m^{-1/2}$ and $\tilde{R}_{mm} = R_{mm} (f_m / f_m)^{1/2}$. The solution of Eq. (3.5) is expressed as

$$\begin{aligned} \sigma_{mm}(t) = & \sum_a \sum_j \sum_\ell (f_m / f_\ell)^{\frac{1}{2}} N_{mj} \frac{1 - \exp[-(\lambda_{jj} - k_{aa})t]}{\lambda_{jj} - k_{aa}} \\ & \times (N^{-1})_{j\ell} k_{\ell a}^{(1)} \exp(-k_{aa}t) \sigma_{aa}(0) , \end{aligned} \quad (3.6)$$

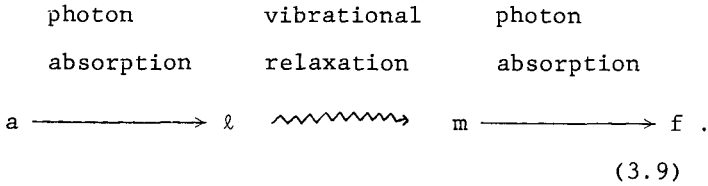
in which N_{mj} and λ_{jj} satisfy the equation

$$(K + \tilde{R})N = N\lambda . \quad (3.7)$$

Substituting Eq. (3.6) into Eq. (3.3) yields the expression for the two-photon transition rate, $J^{(2)}(t)$ after taking summation over the final vibronic levels:

$$\begin{aligned} J^{(2)}(t) = & \sum_f \frac{d\sigma_{ff}(t)}{dt} \\ = & \sum_f \sum_a [k_{fa}^{(2)} + \sum_m \sum_\ell k_{fm}^{(1)} \lambda_{m\ell}(t) k_{\ell a}^{(1)}] \exp(-k_{aa}t) \sigma_{aa}(0) , \end{aligned} \quad (3.8)$$

where the first term involving the simultaneous process, sequential one induced by elastic molecule-bath interactions and their mixing term will be discussed in a subsequent section, and the second term expresses the sequential process induced by vibrational relaxations:



The matrix element, $\lambda_{m\ell}(t)$ is given by

$$\lambda_{m\ell}(t) = (f_m/f_\ell)^{\frac{1}{2}} \sum_j N_{mj} \frac{1 - \exp[-(\lambda_{jj} - k_{aa})t]}{\lambda_{jj}} (N^{-1})_{j\ell} . \quad (3.10)$$

For the steady state in the resonant state, Eq. (3.10) takes the form

$$\lambda_{m\ell}(t \rightarrow \infty) = (f_m/f_\ell)^{\frac{1}{2}} \sum_j N_{mj} \lambda_{jj}^{-1} (N^{-1})_{j\ell} . \quad (3.11)$$

For the time scale of the pulse in which the depopulation of the initial state can be neglected, the transition rate constant in the steady state condition can be written as

$$J^{(2)} = \sum_f \sum_a [k_{fa}^{(2)} + \sum_m \sum_\ell k_{fm}^{(1)} \lambda_m(t \rightarrow \infty) k_{\ell a}^{(1)}] \sigma_{aa}(0) . \quad (3.12)$$

Effects of the vibrational relaxations on a resonant two-photon ionization of molecules have been discussed elsewhere.²² Slow and fast vibrational relaxation cases, compared with the transition rate constant from the resonant to the ionization states, are taken into account.

For the extreme situation in which no vibrational relaxation exists, noting that K is a diagonal matrix and $N_{mj} = \delta_{mj}$, and further for the case in which $\lambda_{jj} > k_{aa}$, we obtain

$$J^{(2)}(t) = \sum_f \sum_a [k_{fa}^{(2)} + \sum_m k_{ma}^{(1)}] \exp(-k_{aa} t) \sigma_{aa}^{(0)} . \quad (3.11)$$

The apparent transition rate constant $k_{ma}^{(1)}$ for the resonant two-photon transition originates from the fact that the transition rate from the resonant to the final state is faster than the excitation rate to the resonant state, and is the rate constant of the rate-determining step if the magnitude of $k_{fa}^{(2)}$ is negligibly small.

Murakami et al.²³ have observed the two-photon resonant four-photon ionization of benzene and the halogen-substituted benzenes. They have concluded that the resonant multiphoton ionization spectra reflect the two-photon absorption spectra of $S_1 + S_0$ transition. This suggests that the rate from the ground to the resonant states mainly contributes to the multiphoton process. This can be interpreted in terms of the expression similar to Eq. (3.11).

III-1B. Structure of two-photon absorption rate constants, $k_{fa}^{(2)}$

In this section, the structure of the two-photon absorption rate constant $k_{fa}^{(2)}$ is discussed. This has the

structure similar to that for resonant light scattering in which both simultaneous (coherent) and sequential (incoherent) processes participate.^{24,25} It is well known that the latter process in the resonant vibrational light scattering is induced by pure dephasing processes related to the initial and resonant states,²⁶⁻³⁰ and the simultaneous and sequential processes can be separated out in the case of the negligibly small dephasing constant between the initial and final states.³¹

It should be noted that there exists a difference in the contribution of the dephasings between the resonant vibrational light scattering and the resonant two-photon transitions (absorption, ionization, etc.). For the former, the dephasing constant between the initial (final) and resonant states, which may be called electronic dephasing constant, and that between the initial and final states, called vibrational dephasing constant, make contribution. For the resonant two-photon transition, on the other hand, both dephasing constant between the initial (final) and resonant states and that between the initial and final states belong to the electronic dephasing constant. When the magnitudes of these dephasing constants are of the same order, the coherent and incoherent processes can not be separated out; a mixing process between two processes participates in the resonant two-photon processes.^{24,31} It is commonly accepted that the magnitude of the vibrational dephasing constant is negligibly small compared with that of the

electronic dephasing constant.

From Eqs. (2.39) and (2.67), the two-photon transition rate constant is given by

$$k_{fa}^{(2)} = 2 \lim_{t \rightarrow \infty} \text{Re} \{ W^{(2A)}(t) + W^{(2B)}(t) + W^{(2C)}(t) \} , \quad (3.12)$$

where $W^{(2A)}(t)$, $W^{(2B)}(t)$, and $W^{(2C)}(t)$ are defined by Eqs. (2.69). In calculating Eq. (3.12), photon-field correlation functions with constant pulse amplitudes with E_1 and E_2 for the first and second lasers neglecting the band widths are considered:

$$\langle E_1^{(+)}(t_i) E_1^{(-)}(t_j) \rangle_R = E_1^2 \exp[i(t_i - t_j)\omega_1] , \quad (3.13a)$$

and

$$\langle E_2^{(+)}(t_i) E_2^{(-)}(t_j) \rangle_R = E_2^2 \exp[i(t_i - t_j)\omega_2] . \quad (3.13b)$$

After substituting Eqs. (3.13) into Eqs. (2.69), carrying out the integration of the resulting expression over the time variables, and taking the limit $t \rightarrow \infty$, the two-photon transition rate constant averaged over the initial vibrational distribution with σ_{aa} , $k^{(2)}$ is expressed as

$$\begin{aligned}
k^{(2)} &= \sum_a \sum_f \sigma_{aa} k_{fa}^{(2)} \\
&= \frac{2}{\hbar^4} E_1^2 E_2^2 \operatorname{Re} \sum_a \sum_f \sigma_{aa} \sum_{m m'} M_{am'}^{(1)} M_{m'f}^{(2)} M_{fm}^{(2)} M_{ma}^{(1)} \\
&\quad \times \left[\frac{1}{(i\Delta\omega_{fa} + \Gamma_{fa})(i\Delta\omega_{fm'} + \Gamma_{fm'}) (i\Delta\omega_{ma} + \Gamma_{ma})} \right. \\
&\quad + \frac{1}{(i\Delta\omega_{ma} + \Gamma_{ma})(i\Delta\omega_{mf} + \Gamma_{mf})(i\Delta\omega_{fm'} + \Gamma_{fm'})} \\
&\quad \left. \times \left(1 + \frac{\Gamma_{fm'} + \Gamma_{mf} - \Gamma_{mm'}}{i\Delta\omega_{mm'} + \Gamma_{mm'}} \right) \right], \quad (3.14)
\end{aligned}$$

where $\Delta\omega_{fa} = \omega_{fa} - \omega_1 - \omega_2$, $\Delta\omega_{ma} = \omega_{ma} - \omega_1$, and $\Delta\omega_{fm'} = \omega_{fm'} - \omega_2$. Equation (3.14) can be classified as

$$k^{(2)} = k^{(2\text{-sim})} + k^{(2\text{-seq})} + k^{(2\text{-mix})}, \quad (3.15)$$

where $k^{(2\text{-sim})}$ represents the transition probability of the simultaneous process, and is given by

$$k^{(2\text{-sim})} = \frac{2}{\hbar^4} E_1^2 E_2^2 \operatorname{Re} \sum_a \sum_f \frac{\sigma_{aa}}{i\Delta\omega_{fa} + \Gamma_{fa}} \left| \sum_m \frac{M_{fm}^{(2)} M_{ma}^{(1)}}{i\Delta\omega_{ma} + \Gamma_{ma}} \right|^2. \quad (3.16)$$

$k^{(2\text{-seq})}$, representing the transition probability of the sequential process, is expressed as

$$\begin{aligned}
k^{(2\text{-seq})} &= \frac{2}{\hbar^4} E_1^2 E_2^2 \operatorname{Re} \sum_a \sum_f \sum_{m m'} (\Gamma_{fm'} + \Gamma_{mf} - \Gamma_{mm'}) \\
&\quad \times \frac{M_{am'}^{(1)} M_{m'f}^{(2)} M_{fm}^{(2)} M_{ma}^{(1)}}{(i\Delta\omega_{ma} + \Gamma_{ma})(i\Delta\omega_{mf} + \Gamma_{mf})(i\Delta\omega_{fm'} + \Gamma_{fm'}) (i\Delta\omega_{mm'} + \Gamma_{mm'})} \\
&\hspace{15em} (3.17)
\end{aligned}$$

and $k^{(2\text{-mix})}$ representing the transition probability of their mixing process is given by

$$\begin{aligned}
 k^{(2\text{-mix})} &= \frac{2}{\hbar^4} E_1^2 E_2^2 \operatorname{Re} \sum_a \sum_f \frac{\sigma_{aa}}{i\Delta\omega_{fa} + \Gamma_{fa}} \sum_{m'} \sum_{m''} \\
 &\times \{ (\Gamma_{fa} + \Gamma_{m'a} - \Gamma_{fm'}) (i\Delta\omega_{mf} + \Gamma_{mf}) + (i\Delta\omega_{fa} + \Gamma_{fa}) \\
 &\times [-i(\Delta\omega_{mf} + \Delta\omega_{m'a}) - \Gamma_{mf} + \Gamma_{m'a}] \} \\
 &\times \frac{M_{am'}(1) M_{m'f}(2) M_{fm''}(2) M_{ma}(1)}{(i\Delta\omega_{ma} + \Gamma_{ma}) (i\Delta\omega_{mf} + \Gamma_{mf}) (i\Delta\omega_{fm''} + \Gamma_{fm''}) (-i\Delta\omega_{m'a} + \Gamma_{m'a})} .
 \end{aligned} \tag{3.18}$$

Effects of laser bandwidths were neglected in the treatment described above. Recently a finite laser bandwidth has been taken into account to discuss the mechanism of the resonant two-photon transitions. If the photon field correlation function $\langle \dots \rangle_R$ is expressed as³²

$$\langle E^{(+)}(t_i) E^{(-)}(t_j) \rangle_R = E^2 \exp[i(t_i - t_j)\omega - |t_i - t_j|\delta\omega] , \tag{3.19}$$

where $\delta\omega$ denotes the laser bandwidth, it can easily be shown that the expression for the rate constant is given from Eq. (3.14) by replacing $\Gamma_{fa} \rightarrow \Gamma_{fa} + \delta\omega_1 + \delta\omega_2$, $\Gamma_{ma} \rightarrow \Gamma_{ma} + \delta\omega_1$, $\Gamma_{fm'} \rightarrow \Gamma_{fm'} + \delta\omega_2$, and so on.

III-1C. Vibronic intensity distributions in resonant two-photon absorptions

One of the resonance effects is revealed in the appearance of vibrational structures in the multiphoton spectra.⁹ This is related to the difference among the potential energy surfaces involved in the multiphoton transition, and can be explained by using the Franck-Condon principle. For example, potential displacements between the initial and resonant states and/or between the resonance and final states as well as those between the initial and final electronic states reflect on the two-photon absorption spectra. This indicates that there exists a difference in the vibronic intensity distribution between the simultaneous and sequential transitions.

In this subsection, analytical expressions for the transition probability of the simultaneous and sequential two-photon absorption processes for a multilevel molecular system are presented within the displaced harmonic oscillator model.²⁴

Let us first consider the simultaneous process shown in Fig. 3.2. The simultaneous two-photon transition probability, $k^{(2\text{-sim})}$ is given by Eq. (3.16). In the Born-Oppenheimer approximation, the molecular state a is expressed as $|a\rangle = |\phi_a\rangle|\theta_a\rangle$, where $|\phi_a\rangle$ and $|\theta_a\rangle$ represent electronic and vibrational eigenvectors of the a th electronic state, respectively. Equation (3.16) can be expressed in

the generating function form as

$$k^{(2\text{-sim})} = \frac{E_1^2 E_2^2}{\hbar^4} |M_{fm}^0 M_{ma}^0|^2 \int_{-\infty}^{\infty} dt \int_0^{\infty} d\tau \int_0^{\infty} d\tau' \exp[-\Gamma_{fa}|t| - \Gamma_{ma}(\tau+\tau') - it(\omega_1+\omega_2) - i(\tau'-\tau)\omega_1] G(\tau, \tau', t) . \quad (3.20)$$

$G(\tau, \tau', t)$, the generating function for the simultaneous two-photon transition, is given by

$$G(\tau, \tau', t) = \sum_a \langle \Theta_a | \sigma_{aa} \exp[-i(t+\tau'-\tau)\hat{H}_a/\hbar] \times \exp[i\hat{H}_m \tau'/\hbar] \exp[i\hat{H}_f t/\hbar] \exp[-i\hat{H}_m \tau/\hbar] | \Theta_a \rangle , \quad (3.21)$$

where \hat{H} represent the vibronic Hamiltonians of the relevant states. In deriving Eq. (3.20), polarization effects were neglected, and the Condon approximation was used:

$M_{fm}^0 = \langle \Phi_f^0 | e \mathbf{r} | \Phi_m^0 \rangle$ where $\Phi_m^0(\Phi_f^0)$ is the electronic wave function for the resonant (final) state, evaluated at the equilibrium position in the electronic ground state. For simplicity, let us consider a displaced harmonic oscillator model in which the vibronic Hamiltonians of the initial, resonant, and final electronic states are, respectively, written as

$$\hat{H}_a = \frac{\hbar\omega}{2} (\hat{p}^2 + q^2) , \quad (3.22a)$$

$$\hat{H}_m = \frac{\hbar\omega}{2} [\hat{p}^2 + (q - \Delta_{ma})^2] + \epsilon_m^0 , \quad (3.22b)$$

and

$$\hat{H}_f = \frac{\hbar\omega}{2} [\hat{p}^2 + (q - \Delta_{fa})^2] + \epsilon_f^0, \quad (3.22c)$$

where ω is the harmonic frequency, q and \hat{p} are the dimensionless nuclear coordinate and the conjugated momentum. Δ_{ma} represents the dimensionless displacement between the equilibrium points in the resonant and ground electronic states, and ϵ_m^0 is the electronic energy gap between the bottoms in the two electronic states. In this model, Eq. (3.20) can be expressed in the analytical form as

$$\begin{aligned} k^{(2-sim)} &= \frac{2E_1^2 E_2^2}{\hbar^4} |M_{fm}^0 M_{ma}^0|^2 \exp[-(\bar{n} + \frac{1}{2})(\Delta_{ma}^2 + \Delta_{fm}^2)] \\ &\times \sum_{k=0}^{\infty} \sum_{\ell=0}^{\infty} \frac{(\bar{n}+1)^k n^\ell}{k! \ell!} \frac{\Gamma_{fa}}{\{\omega_1 + \omega_2 - \frac{\epsilon_f^0}{\hbar} - (k-\ell)\omega\}^2 + \Gamma_{fa}^2} \\ &\times \left| \sum_{p=0}^k \sum_{q=0}^{\ell} \sum_{r=0}^{\infty} \sum_{s=0}^{\infty} \binom{k}{p} \binom{\ell}{q} \left\{ -(\bar{n}+1) \frac{\Delta_{fm} \Delta_{ma}}{2} \right\}^r \right. \\ &\times \left. \left(-\bar{n} \frac{\Delta_{fm} \Delta_{ma}}{2} \right)^s \left(\frac{\Delta_{fm}}{\sqrt{2}} \right)^{k-p+\ell-q} \left(\frac{\Delta_{ma}}{\sqrt{2}} \right)^{p+q} \frac{1}{r! s!} \right. \\ &\times \left. \frac{1}{i \left\{ \frac{\epsilon_m^0}{\hbar} - \omega_1 + (p-q+r-s)\omega \right\} + \Gamma_{ma}} \right|^2. \end{aligned} \quad (3.23)$$

In the low temperature limit for the molecules, Eq. (3.23) reduces to

$$\begin{aligned}
k^{(2\text{-sim})} &= \frac{2E_1^2 E_2^2}{\hbar^4} |M_{fm}^0 M_{ma}^0|^2 \exp\left[-\frac{1}{2}(\Delta_{ma}^2 + \Delta_{fm}^2)\right] \\
&\times \sum_{\ell=0}^{\infty} \frac{\Gamma_{fa}}{\ell! \left\{ (\epsilon_f^0/\hbar + \ell\omega - \omega_1 - \omega_2)^2 + \Gamma_{fa}^2 \right\}} \\
&\times \left| \sum_{j=0}^{\ell} \binom{\ell}{j} \left(\frac{\Delta_{fm}}{\sqrt{2}}\right)^j \left(\frac{\Delta_{ma}}{\sqrt{2}}\right)^{\ell-j} \right. \\
&\times \left. \sum_{k=0}^{\infty} \frac{(-1)^k (\Delta_{fm} \Delta_{ma}/2)^k}{k! \left\{ i(\epsilon_m^0/\hbar - \omega_1 - j\omega + \ell\omega + k\omega) + \Gamma_{ma} \right\}} \right|^2. \quad (3.24)
\end{aligned}$$

An expression for the vibronic intensity distribution of the sequential two-photon absorption in the Born-Oppenheimer approximation can be derived from Eq. (3.17). For simplicity, the following approximation is adopted, $(i\omega_{mm} + \Gamma_{mm})^{-1} \simeq \delta_{mm}/\Gamma_{mm}$, which means neglect of interference effects between the vibronic levels in the resonant state. In this approximation, Eq. (3.17) can be written as

$$k^{(2\text{-seq})} \propto \frac{2\Gamma_{mf} - \Gamma_{mm}}{\Gamma_{mm}\Gamma_{mf}} \sum_m I_{a \rightarrow m}(\omega_1) I_{m \rightarrow f}(\omega_2), \quad (3.25)$$

where $I_{a \rightarrow m}(\omega_1)$ and $I_{m \rightarrow f}(\omega_2)$ represent the line shape function of the absorption from the electronic ground state to a single vibronic level m in the resonant state and that from this level to the final electronic state, and they are given by

$$I_{a \rightarrow m}(\omega_1) = \sum_a \sigma_{aa} \frac{\Gamma_{ma} |\langle \theta_a | \theta_m \rangle|^2}{\Delta\omega_{ma}^2 + \Gamma_{ma}^2}, \quad (3.26a)$$

and

$$I_{m \rightarrow f}(\omega_2) = \sum_f \frac{\Gamma_{mf} |\langle \Theta_m | \Theta_f \rangle|^2}{\Delta_{mf}^2 + \Gamma_{mf}^2}, \quad (3.26b)$$

respectively.

In a displaced harmonic oscillator model, an analytical expression in the low temperature limit can be obtained as

$$\begin{aligned} k^{(2\text{-seq})} &\propto \frac{(2\Gamma_{mf} - \Gamma_{mm})\Gamma_{ma}}{\Gamma_{mm}} \sum_{k=0}^{\infty} \frac{\left(\frac{\Delta_{ma}^2}{2}\right)^k \exp\left[-\frac{\Delta_{ma}^2}{2}\right]}{k! \left\{ (\epsilon_m^0 / \hbar + k\omega - \omega_1)^2 + \Gamma_{ma}^2 \right\}} \\ &\times \sum_{j=0}^k \frac{k!}{(k-j)!(j!)} \left(\frac{\Delta_{ma}^2}{2}\right)^j \exp\left[-\frac{\Delta_{fm}^2}{2}\right] \\ &\times \sum_{p=0}^{2j} \binom{2j}{p} (-1)^p \sum_{\ell=0}^{\infty} \frac{\left(\frac{\Delta_{fm}^2}{2}\right)^\ell}{\ell! \left\{ (\epsilon_f^0 - \epsilon_m^0) / \hbar - \omega_2 + j\omega - p\omega + \ell\omega \right\}^2 + \Gamma_{mf}^2}. \end{aligned} \quad (3.26c)$$

To illustrate the difference in the vibronic intensity distribution between the simultaneous and sequential two-photon transition, model calculations of the vibronic structures are performed by using the analytical expressions derived above. In Figs. 3.3 and 3.4, the vibronic intensity distributions in the case of excitation of the detuning frequency $\omega_1 - \epsilon_m^0 / \hbar = -200 \text{ cm}^{-1}$ are shown as a function of $\omega_2 - (\epsilon_f^0 - \epsilon_m^0) / \hbar$. The dimensionless displacement between the resonant and final state, Δ_{fm} was taken to be 2.0 and 0 for Figs. 3.3 and 3.4, respectively, and $\Delta_{ma} = 1.6$. The dephasing

constant $\Gamma_{ma} = 5.0$, $\Gamma_{fa} = 5.0$, and $\Gamma_{fm} = 10.0$, and the population decay constant $\Gamma_{mm} = 10.0$ were used. The dual structure in these figures reflects the simultaneous and sequential mechanisms: the bands whose peak locates at the integral multiple on the abscissa correspond to those originated from the sequential two-photon transition, and the other bands correspond to those originated from the simultaneous transition. The vibronic intensity distribution of the sequential transition depends on the sum of the transition probabilities from the vibronic levels in the resonant state to the final vibronic levels. On the other hand, the vibronic intensity distribution of the simultaneous transition is not expressed by a simple combination of the optical transitions such as that of the sequential one.

III-1D. Effects of the dephasings in three-photon absorptions

In this subsection, effects of the dephasings, especially pure electronic dephasing on the resonant three-photon absorption are described, and it is shown that sequential three-photon transitions can be induced by the pure electronic dephasing.

The three-photon transition probability can be expressed in terms of ten different time-evolution diagrams. The transition probability averaged over the initial vibrational distribution $k^{(3)}$ can be written as

$$\begin{aligned}
k^{(3)} \propto \text{Re} \sum_a \sum_f \sigma_{aa} \sum_k \sum_{k'} \sum_m \sum_{m'} M_{am}^{(1)} M_{k'm}^{(2)} M_{m'f}^{(3)} M_{fm}^{(3)} M_{mk}^{(2)} \\
\times M_{ka}^{(1)} [G_{af} G_{ak'} G_{am} G_{mf} G_{kf} \\
+ G_{mf} (G_{ka} + G_{ak'}) (G_{km} + G_{mk'}) G_{mm'} G_{kk'} \\
+ G_{mf} (G_{ka} G_{mk'} G_{ma} + G_{ak'} G_{am'} G_{km'}) G_{mm'} \\
+ G_{mf} G_{kf} G_{km'} (G_{ka} + G_{ak'}) G_{kk'} \\
+ G_{mf} G_{ak'} G_{kf} G_{am'} G_{km'}] , \quad (3.27)
\end{aligned}$$

where k and k' , and m and m' specify the vibronic levels in the same electronic states, respectively.

$$G_{fa} = \{i(\omega_{fa} - 3\omega_R) + \Gamma_{fa}\}^{-1} , \quad (3.28)$$

and the other matrix elements of G can be expressed in the similar way. Here it has been assumed that the molecules have been excited by three photons with an identical frequency, ω_R .

For a nonresonant three-photon absorption, Eq. (3.27) can approximately be expressed as

$$k^{(3\text{-sim})} \propto \text{Re} \sum_a \sum_f \sigma_{aa} G_{af} \left| \sum_k \sum_m M_{ak}^{(1)} G_{ak} M_{km}^{(2)} G_{am} M_{mf}^{(3)} \right|^2 , \quad (3.29)$$

which can be assigned to the transition probability for the simultaneous three-photon transition.

For a detailed discussion of the dephasing effects a three-photon absorption in which resonance occurs on the absorption of the second photon, so-called (2+1) process shown in Fig. 3.5 will be considered. This process can be seen in multiphoton transitions of molecules such as iodine,³⁴⁻³⁶ nitric oxide,³⁷ trans 1-3-butadiene,³⁸ benzene,³⁹ van der Waals complexes,⁴⁰ etc. Setting $m = m'$ in Eq. (3.27) yields an approximate expression for the transition probability appropriate for the (2+1) process:

$$k^{(2+1)} \simeq k^{(2+1, \text{sim})} + k^{(2+1, \text{seq})} + k^{(2+1, \text{mix})} \quad , \quad (3.30)$$

where

$$k^{(2+1, \text{sim})} \propto \text{Re} \sum_a \sum_f \sigma_{aa} G_{af} \sum_m |M_{fm}(3) G_{am}|^2 \left| \sum_k M_{ak}(1) G_{ak} M_{km}(2) \right|^2 \quad , \quad (3.31)$$

$$k^{(2+1, \text{seq})} \propto \sum_a \sum_f \sigma_{aa} \sum_m \frac{2\Gamma_{ma}^{(d)} + \Gamma_{aa}}{\Gamma_{mm} \Gamma_{ma}} |M_{fm}(3)|^2 \text{Re} G_{mf} \text{Re} G_{am} \\ \times \left| \sum_k M_{ak}(1) G_{ak} M_{km}(2) \right|^2 \quad , \quad (3.32)$$

$$k^{(2+1, \text{mix})} \propto \sum_a \sum_f \sigma_{aa} \sum_m |M_{fm}(3)|^2 (\Gamma_{fa} + \Gamma_{ma} - \Gamma_{fm}) \\ \times \text{Re} G_{af} G_{mf} |G_{am}|^2 \left| \sum_k M_{ak}(1) G_{ak} M_{km}(2) \right|^2 \quad . \quad (3.33)$$

Equation (3.31) represents the simultaneous (2+1) process. Equation (3.32) represents the sequential (2+1) process which mainly originates from an electronic pure dephasing between the initial and resonant states because the third photon is absorbed from the resonant state disturbed by the elastic interaction between the molecule and heat bath during the two-photon absorption. Γ_{aa} may make no any significant contribution. Equation (3.33) describes mixing effects of the processes expressed in terms of Eqs. (3.31) and (3.32). In the case in which the condition among the dephasing constants, $\Gamma_{fm} \simeq \Gamma_{ma} > \Gamma_{af}$ is satisfied, the mixing term can be omitted compared with $k^{(2+1, \text{sim})}$ and $k^{(2+1, \text{seq})}$.

In a previous paper,³³ we have discussed about the possibility of identifying the vibronic bands characterized by the simultaneous or sequential processes in the resonant (2+1) multiphoton absorption spectrum using a single laser beam of its frequency ω_R . The band peaks appearing in the three-photon absorption spectrum as a function of ω_R (or $2\omega_R$, $3\omega_R$) are mainly determined by the following resonance conditions: $\Delta\omega_{af} = 3\omega_R - \omega_{fa} = 0$ and $\Delta\omega_{mf} = \omega_R - \omega_{mf} = 0$ for the simultaneous and sequential processes, respectively, in addition to the resonance condition of the two-photon absorption, $\Delta\omega_{am} = 2\omega_R - \omega_{am} = 0$ for both processes.

To demonstrate the spectral features reflected in the (2+1) absorption spectrum, a model calculation of the vibronic intensity distributions has been carried out within

a displaced harmonic oscillator approximation. Analytical expressions for the transition probabilities of the (2+1) processes have been derived and used.³³ A result of the model calculation is shown in Fig. 3.6 in which vibronic bands due to the simultaneous and sequential (2+1) processes are denoted by a and b, respectively. The abscissa is expressed in terms of $2\omega_R$ and $3\omega_R$. The molecular parameters used are $\Delta_{ka} = 0$, $\Delta_{fm} = 0$, and $\Delta_{mk} = \Delta_{ma} = 0.1$ for the dimensionless displacements, $\omega = 500 \text{ cm}^{-1}$ for the molecular vibrational frequency, and $\omega_{fa} = 72180$, $\omega_{ma}^0 = 72180$, $\omega_{ma}^0 = 48000$, and $\omega_{ka}^0 = 32000 \text{ cm}^{-1}$ for the electronic energy gaps. The dephasing constants are $\Gamma_{aa} = 0$, $\Gamma_{kk} = 0$, $\Gamma_{ff} = 0.2$ and $\Gamma_{mm} = 2.0 \text{ cm}^{-1}$, $\Gamma_{ma}^{(d)} = 10.0$, $\Gamma_{fm}^{(d)} = 10.0$, $\Gamma_{fa}^{(d)} = 10.0$, $\Gamma_{ka}^{(d)} = 0$, and $\Gamma_{fa}^{(d)} = 2.0 \text{ cm}^{-1}$. One of the prominent features in the spectrum is the existence of the resonance band located at $2\omega_R = 48360 \text{ cm}^{-1}$. This band can be assigned to that originating from the sequential process because the third photon whose frequency of $\omega_R = \omega_{fm} = 24180 \text{ cm}^{-1}$ is absorbed from the relaxed vibronic level in the resonant state m to the final state f as shown in Fig. 3.7.

III-2. Dephasing effects in quantum beats in molecular fluorescence

Quantum beats in the fluorescence of molecules excited by a coherent pulse laser have recently been reported by many authors.⁴¹⁻⁴⁸ By analyzing the quantum beats in the

fluorescence one can investigate the magnitude of the interaction between the molecule and a perturber of the heat bath as well as the mechanism of the inter/intra electronic state couplings in electronically excited states.⁴⁹ For molecules belonging to the intermediate case, effects of collisional dephasing make an important contribution to the time-dependent behavior of the excited states. In this section, the collision effects resulting from both elastic and inelastic scattering processes between the molecule and perturber are theoretically studied based on the expressions of the reduced matrix elements derived in Sec. II. The dephasing effects are taken into account in the Markoff approximation. A non-Markoff theory of quantum beats will be presented elsewhere.⁵⁰

The fluorescence intensity at time t , $I(t)$ from m and n levels after a coherent excitation is given by

$$I(t) = K \sum_{\mathbf{f}} \sum_{\mathbf{m}} |M_{\mathbf{mf}}|^2 \sigma_{\mathbf{mm}}(t) + K \sum_{\mathbf{f}} \sum_{\mathbf{m}} \sum_{\mathbf{n}} \underset{(m \neq n)}{M_{\mathbf{nf}} M_{\mathbf{fm}}} \sigma_{\mathbf{mn}}(t), \quad (3.34)$$

where K is a constant involving the frequency of the emitted photon, $\sigma(t)$ whose matrix elements are given by Eq. (2.61) is the molecular density matrix representing the time evolution of the excited states, and \mathbf{f} specifies the final molecular states, respectively.

In order to investigate the dephasing effects, a model calculation of the quantum beats is carried out in the two-

level model for the excited (fluorescent) state.¹⁷ The following correlation function for the incident photon field is used:

$$\langle E^{(+)}(t_1)E^{(-)}(t_2) \rangle = \bar{\varepsilon}(t_1)\bar{\varepsilon}(t_2)\exp[i\omega_I(t_1-t_2)]\tilde{G}(t_1-t_2) , \quad (3.35)$$

where the stationary function \tilde{G} is assumed to take the form

$$\tilde{G}(t_1-t_2) = \exp[-|t_1-t_2|\Gamma'] , \quad (3.36)$$

in which $1/\Gamma'$ represents the correlation time of the photon source, and $\bar{\varepsilon}(t)$ is the pulse amplitude and is assumed to be given by

$$\begin{aligned} \bar{\varepsilon}(t) &= \exp(\gamma_1 t/2) , & t < 0 , \\ &= 1 , & 0 \leq t \leq \tau_p , \\ &= \exp[-\gamma_2(t-\tau_p)/2] , & \tau_p < t . \end{aligned} \quad (3.37)$$

In Figs. 3.8a and 3.8b, the fluorescence intensity denoted by solid line is calculated together with the degree of the molecular coherence between the two excited states (broken line), $C(m,n)$ defined by Eq. (2.62). In these figures, the effect of the pure dephasing constant between the excited states, $\Gamma_{mn}^{(d)}$ is shown. In Figs. 3.8a and 3.8b, $\Gamma_{mn}^{(d)} = 0$ and $\Gamma_{mn}^{(d)} = 0.2\omega_{mn}$ were used. Other

constants used were $\Gamma' = 0$, $\tau_p = 3.14/\omega_{mn}$, $\Gamma_{ma}^{(d)} = \Gamma_{na}^{(d)} = 0.1\omega_{mn}$, $\Gamma_{mm} = \Gamma_{nn} = 0.1\omega_{mn}$, $\Gamma_{aa} = \Gamma_{ff} = 0$, $M_{ma} = M_{na} = M_{mf} = M_{nf}$, $\gamma_1 = \gamma_2 = 10.0\omega_{mn}$, and $\omega_I - \omega_n = 0.5\omega_{mn}$ as an excitation condition. The decay of the quantum beat after the pulse duration in Fig. 3.3 a is due to the population decay constants Γ_{mm} and Γ_{nn} . From both figures, we can see that the electronic pure dephasing constant $\Gamma_{ma}^{(d)}$ does not attenuate $C(m,n)$ after the pulse duration. The vibrational pure dephasing constant between the excited states, on the other hand, attenuates $C(m,n)$ during and after the pulse duration as well as the intensity of the quantum beat. Effects of the photon field coherence have also been investigated;¹⁷ Γ' shows the same dependence on the fluorescence intensity as that of the electronic dephasing between the initial and excited states, i.e., during the pulse duration Γ' operates.

III-3. Time-resolved resonance Raman scattering from molecules with a nonequilibrium vibronic distribution

In this section, a theoretical treatment of the time-resolved resonance Raman scattering (RRS) from vibronic levels of a molecule in a nonequilibrium condition is presented.^{51,52} Time-resolved resonance Raman spectroscopy is now widely applied to studying dynamics of short-lived vibronically excited molecules such as photochemical and biological intermediates and so on.⁵³⁻⁵⁶ The spectroscopy basically consists of the

measurement of the time-dependent population of the vibronically excited states by controlling the time delay between excitation laser and the probe Raman scattering. The vibrational spectra of the time-resolved RRS depend on the initial nonequilibrium vibronic distribution which is produced by optical excitations, electronic relaxations, photochemical reactions following the optical excitation, etc., and on its relaxation mechanism which governs the subsequent population change.

Theoretical treatments of the time-resolved RRS from nonequilibrium species have been reported by Luzzi and Vasconcellos,⁵⁷ and Vasconcellos and Luzzi.⁵⁸ They have developed the theory of the time-resolved Raman scattering from a highly photo-excited semi-conductor plasma by using the Zubarev nonequilibrium ensemble method. In this section, the generating function method^{59,60} is applied to deriving an expression for the RRS differential cross section.

Let us consider a time-resolved RRS from initial vibronic states $a\{v\}$ to the final states $a\{v'\}$ via resonant electronic states. In the case in which the pumping and probe lasers are independent each other, that is, coherent effects can be neglected, and the probe Raman laser does not change the population, the differential cross section in a solid angle $d\Omega$ per unit scattered photon frequency ω_2 , $d^2\sigma(\omega_1, \omega_2, t)/d\Omega d\omega_2$ is defined as

$$\frac{d^2\sigma(\omega_1, \omega_2, t)}{d\Omega d\omega_2} = \sum_v \rho_v(t) \frac{d^2\sigma_v(\omega_1, \omega_2)}{d\Omega d\omega_2}, \quad (3.38)$$

where $\rho_v(t)$ represents the time-dependent vibronic distribution of the initial electronic state and is determined by solving the master equation. In Eq.(3.38), ω_1 is the incident photon frequency, and $d^2\sigma_v(\omega_1, \omega_2)/d\Omega d\omega_2$ is the RRS differential cross section from single vibronic level (SVL) v . The differential cross section from the SVL is given by

$$\begin{aligned} \frac{d^2\sigma_v(\omega_1, \omega_2)}{d\Omega d\omega_2} &= C\omega_1\omega_2^3 \sum_{v'} \frac{\Gamma_{av',av}}{(\omega_{av';av} - \omega_1 + \omega_2)^2 + \Gamma_{av',av}^2} \\ &\times \left| \sum_m \frac{M_{av',bm}^{(2)} M_{bm,av}^{(1)}}{i(\omega_{bm,av} - \omega_1) + \Gamma_{bm,av}} \right|^2, \end{aligned} \quad (3.39)$$

where $C=(2\pi\hbar^2\epsilon_0c^4)^{-1}$. In the Born-oppenheimer and the Condon approximations, Eq.(3.39) can be rewritten in terms of the generating function as

$$\begin{aligned} \frac{d^2\sigma_v(\omega_1, \omega_2)}{d\Omega d\omega_2} &= \frac{C}{2} \omega_1\omega_2^3 |M_{ab}^0(2)M_{ba}^0(1)|^2 \int_0^\infty d\tau \int_0^\infty d\tau' \int_{-\infty}^\infty d\xi \\ &\times \exp[i\xi(\omega_1 - \omega_2) + i\omega_1(\tau' - \tau) - \Gamma_{ba}(\tau + \tau') - \Gamma_{v,v}|\xi|] G_v(\tau, \tau', \xi), \end{aligned} \quad (3.40)$$

where the generating function for the single vibronic level RRS, $G(\tau, \tau', \xi)$ is expressed as

$$G_{\mathbf{v}}(\tau, \tau', \xi) = \langle \mathbf{v} | \exp[i\hat{H}_{\mathbf{b}}\tau/\hbar] \exp[-i\hat{H}_{\mathbf{a}}\xi/\hbar] \exp[-i\hat{H}_{\mathbf{b}}\tau'/\hbar] \\ \times \exp[i\hat{H}_{\mathbf{a}}(\xi - \tau + \tau')/\hbar] | \mathbf{v} \rangle. \quad (3.41)$$

In Eq. (3.41), the vibrational quantum number dependence of the dephasing constants has been omitted, that is $\Gamma_{\mathbf{b}\mathbf{a}}$ and $\Gamma_{\mathbf{v}\mathbf{v}}$ are the average electronic and vibrational dephasing constants, respectively. $\hat{H}_{\mathbf{a}}$ and $\hat{H}_{\mathbf{b}}$ in Eq. (3.41) represent the vibrational Hamiltonians of the electronic states, \mathbf{a} and \mathbf{b} , respectively. For simplicity, we restrict ourselves to a model Hamiltonian for a displaced harmonic oscillator with frequency ω , dimensionless displacement Δ , and electronic energy gap ϵ^0 . In this model, the generating function for the single vibronic RRS is given by⁵¹

$$G_{\mathbf{v}}(\tau, \tau', \xi) = \exp[i\epsilon^0(\tau - \tau')/\hbar + \frac{\Delta}{2} \{ \exp(i\omega\tau) - 1 \} \\ + \frac{\Delta}{2} \{ \exp(-i\omega\tau') - 1 \} + \lambda^*(\tau)\lambda(\tau') \exp(-i\omega\xi)] L_{\mathbf{v}}(|\alpha(\tau, \tau', \xi)|^2), \quad (3.42)$$

in which $L_{\mathbf{v}}$ is the Laguerre polynomials,

$$\alpha(\tau, \tau', \xi) = \lambda(\tau) - \lambda(\tau') \exp(-i\omega\xi) , \quad (3.43)$$

and

$$\lambda(\tau) = \frac{\Delta}{\sqrt{2}} \{1 - \exp(-i\omega\tau)\} . \quad (3.44)$$

Substituting Eq.(3.40) with Eq.(3.42) into Eq.(3.38) yields

$$\begin{aligned} \frac{d^2\sigma(\omega_1, \omega_2, t)}{d\Omega d\omega_2} &= \frac{c}{2} \omega_1 \omega_2^3 |M_{ab}^0(2)M_{ba}^0(1)|^2 \int_0^\infty d\tau \int_0^\infty d\tau' \int_{-\infty}^\infty d\xi \\ &\times \exp[i\xi(\omega_1 - \omega_2) + i\omega_1(\tau' - \tau) - \Gamma_{ba}(\tau + \tau') - \Gamma_{v,v}|\xi|] G(\tau, \tau', \xi; t), \end{aligned} \quad (3.45)$$

where $G(\tau, \tau', \xi; t)$ is the generating function for the time-resolved RRS, and is defined as

$$G(\tau, \tau', \xi; t) = \sum_v \rho_v(t) G_v(\tau, \tau', \xi) . \quad (3.46)$$

Let us consider a time-resolved RRS from molecules in which the vibronic distribution is prepared only at level v_0 at $t=0$ (single vibronic level distribution, and relaxes by undergoing both electronic and collisional vibrational relaxations:



If these relaxation constants are assumed to be a linear function of the vibrational quantum number v , that is, $k_v^c = vk_c$ and $k_v^e = vk_e$, the single vibronic distribution at time t , $\rho_v(t)$ is given by⁶¹

$$\rho_v(t) = \rho_{v_0}(0) \frac{v_0!}{v!(v_0-v)!} \left[\frac{k_c}{k_c+k_e} \{1 - \exp[-(k_c+k_e)t]\} \right]^{v_0-v} \times \exp[-v(k_c+k_e)t] , \quad (3.47)$$

where $\rho_{v_0}(0)$ is the density of the v_0 vibronic state at $t=0$. Substituting Eq.(3.47) into Eq.(3.46) and taking summation over v in the resulting expression, we can obtain the expression for the generating function. Substitution of the expression for the generating function into Eq.(3.45) yields the final expression for the time-resolved RRS from the SVL excited molecules as

$$\frac{d^2 \sigma(\omega_1, \omega_2, t)}{d\Omega d\omega_2} = C \omega_1 \omega_2^3 |M_{ab}^0(2) M_{ba}^0(1)|^2 \rho_{v_0}(0) \sum_{j=0}^{\infty} \sum_{n=0}^{v_0} \sum_{p=0}^n \sum_{q=0}^n$$

$$\begin{aligned}
& \times \frac{(-1)^{p+q}}{j! n!} \binom{v_0}{n} \binom{n}{p} \binom{n}{q} \left\{ \frac{k_c}{k_c + k_e} + \frac{k_e}{k_c + k_e} \exp[-(k_c + k_e)t] \right\} v_0^{-n} \\
& \times \exp[-n(k_c + k_e)t] \frac{\Gamma_{v',v}}{[\{\omega_1 - \omega_2 + \omega(n-p-q-j)\}^2 + \Gamma_{v',v}^2]} \\
& \times F(\omega_1)^{(p+j, n-q)} F(\omega_1)^{*(q+j, n-p)}, \tag{3.48}
\end{aligned}$$

where

$$F(\omega_1)^{(k, \ell)} = \int_0^\infty d\tau \{ \kappa^*(\tau) \}^k \{ \lambda(\tau) \}^\ell \exp[i(\varepsilon^0/\hbar - \omega_1)\tau + \frac{\Delta}{2}(e^{i\omega\tau} - 1) - \Gamma_{ba}\tau]. \tag{3.49}$$

This function can be evaluated by using a numerical integration or analytically: the analytical expression is given by

$$\begin{aligned}
F(\omega_1)^{(k, \ell)} &= \exp\left(-\frac{\Delta^2}{2}\right) \left(\frac{\Delta}{\sqrt{2}}\right)^{k+\ell} \sum_{n=0}^{\infty} \sum_{r=0}^k \sum_{u=0}^{\ell} \frac{(-1)^{r+u}}{n!} \\
& \times \left(-\frac{\Delta^2}{2}\right)^n \binom{k}{r} \binom{\ell}{u} \frac{1}{i\{\omega_1 - \varepsilon^0/\hbar + (u-r-n)\omega\} + \Gamma_{ma}}. \tag{3.50}
\end{aligned}$$

To demonstrate the time-dependence of the vibrational intensity of the RRS in the case of the single vibrational level distribution as the initial distribution, a model calculation of the Raman spectra by using Eq.(3.46) has been performed. Figure 3.9 shows the calculated Raman spectra of the model molecule initially excited to $v_0=3$ level with potential displacement $\Delta=1.0$, vibrational frequency $\omega=100 \text{ cm}^{-1}$. $\epsilon^0/\hbar - \omega_1 = 300 \text{ cm}^{-1}$ is taken as the excitation condition. The ordinate I denotes the Raman intensity relative to the maximum band intensity without the optical frequency factors $\omega_1 \omega_2^3$, and $\Gamma_{\text{ma}}=100 \text{ cm}^{-1}$ and $\Gamma_{\text{v,v}}=50 \text{ cm}^{-1}$ are taken as the dephasing constants. This figure represents the calculated Raman spectra in which the contribution of the electronic relaxation can be neglected compared with that of the collisional vibrational relaxation, that is, $k_e=0$. The solid, dotted-broken and broken lines denote the Raman spectra at $k_c t=0, 0.2$, and 0.4 , respectively. It should be noted that the first through third order anti-Stokes Raman bands make a significant contribution to the spectra. The appearance of the anti-Stokes bands is mainly related to which vibronic level is initially prepared. We can see that because of the vibrational relaxation effect the Raman intensities of both anti-Stokes and Stokes bands decrease, and, on the other hand, the Rayleigh band intensity increases as $k_c t$ increases.

So far time-resolved RRS from a SVL system has been presented. Analysis for the time-resolved RRS from molecules characterized by other initial vibronic distributions, such as Poisson and canonical distribution have been reported.^{51,52}

A model calculation of the excitation profiles of the time-resolved RRS from molecules with nonequilibrium distributions has been given in Ref.52. The results of the calculation indicate that the anti-Stokes Raman bands make a significant contribution to the resonance Raman scattering from the nonequilibrium vibronic distributions. It is suggested that measurement of the excitation profiles are useful for analyzing the nonequilibrium distribution initially prepared and the subsequent relaxation mechanism.

In summary, in this chapter, a kinetic equation for the multiphoton transition of molecules and the expressions for the transition probabilities have been derived based on the master equation approach in which dephasing effects are considered together with the molecule-photon interaction. A two-photon transition probability via coherently excited vibronic levels has been formulated. Mechanisms of the multiphoton transition have been investigated; sequential multiphoton transitions induced by the electronic dephasings are predicted for the resonant two- and three-photon absorptions. An expression for the vibronic intensity distribution for the two-photon transition, which depends on its mechanism, has been evaluated within the Born-Oppenheimer approximation. Effects of the vibrational relaxations for a resonant two-photon transition, and dephasing effects in quantum beats in molecular fluorescence have been investigated.

It is shown that the time-resolved RRS may play an important role in studying relaxation mechanisms of the molecule with a nonequilibrium distribution.

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Figure captions

Fig.2.1. Diagrammatic representations of the time evolution of ket and bra vectors related to the one-photon absorption. The diagram in the left-hand side and that in the right-hand side correspond to the first and second terms in Eq.(2.61), respectively.

Fig.2.2. Diagrammatic representations of the ket and bra vectors for a two-photon absorption via coherently excited vibronic levels. Figures 2.2a ,2.2b, and 2.2c correspond to the time evolution in Eqs.(2.69a),(2.69b),and(2.69c), respectively.

Fig.3.2. A simultaneous two-photon transition of a molecule in the displaced harmonic potential model.

Fig.3.3 The calculated vibronic intensity distribution for the two-photon absorption as a function of $\omega_2 - (\epsilon_f^0 - \epsilon_m^0)/\hbar$ in the case of $\Delta_{fm} = 2.0$. The doublet structure reflects the simultaneous and sequential mechanisms; the bands whose peak locates at the integral multiple on the abscissa correspond to those originated from the sequential mechanism, and the other bands correspond to those originated from the simultaneous mechanism.

Fig.3.4. The calculated vibronic intensity distribution for the two-photon absorption in the case of $\Delta_{fm} = 0$.

Fig.3.5 Resonant (2+1) and (1+2) three-photon absorption processes. {m} and {k} represent the resonant intermediate and the virtual states, respectively.

Fig.3.6. The calculated vibronic intensity distribution for a resonant (2 + 1) absorption process. The vibronic bands denoted by a and b mainly originate from the rate constants, $k^{(2+1, sim)}$ and $k^{(2+1, seq)}$, respectively.

Fig.3.7. The mechanism of the sequential absorption induced by the electronic dephasing process related to Fig.3.6.

Fig.3.8a. The effect of the pure electronic dephasings $\Gamma_{ma}^{(d)}$ and $\Gamma_{na}^{(d)}$ on fluorescence intensity $I(t)$ and the degree of molecular coherence $C(m,n)$. The solid and broken lines represent $I(t)$, and $C(m,n)$, respectively.

Fig.3.8b. The effect of the pure dephasing $\Gamma_{mn}^{(d)}$ on $I(t)$, and $C(m,n)$.

Fig.3.9. The calculated time-resolved Raman spectra of the model molecule with single vibronic distribution $v_0=3$. The solid, dotted-broken, and broken lines denote the Raman spectra at $k_c t=0, 0.2, \text{ and } 0.4$, respectively.

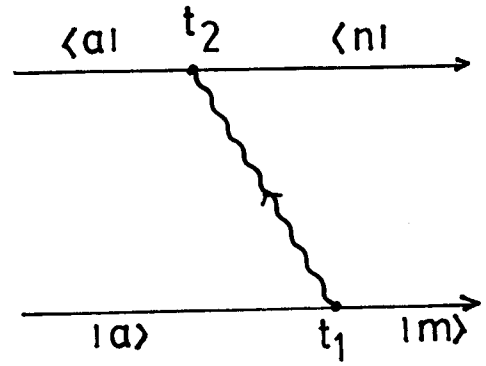
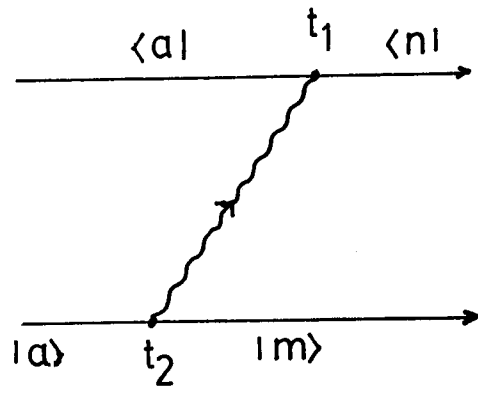
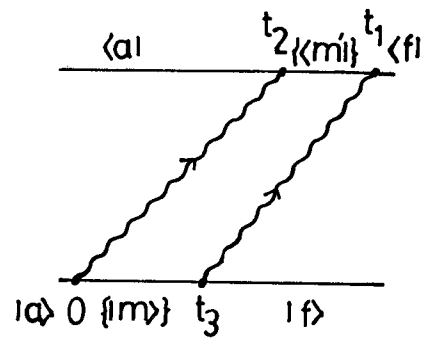
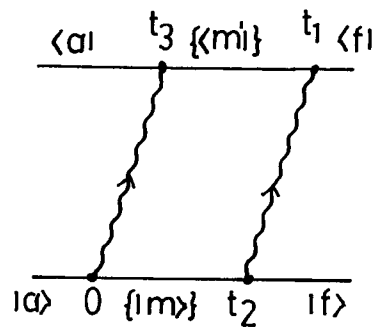


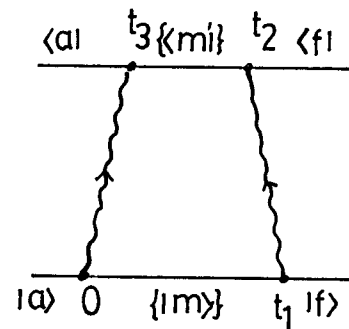
Fig. 2.1



(2.2a)



(2.2b)



(2.2c)

Fig. 2.2

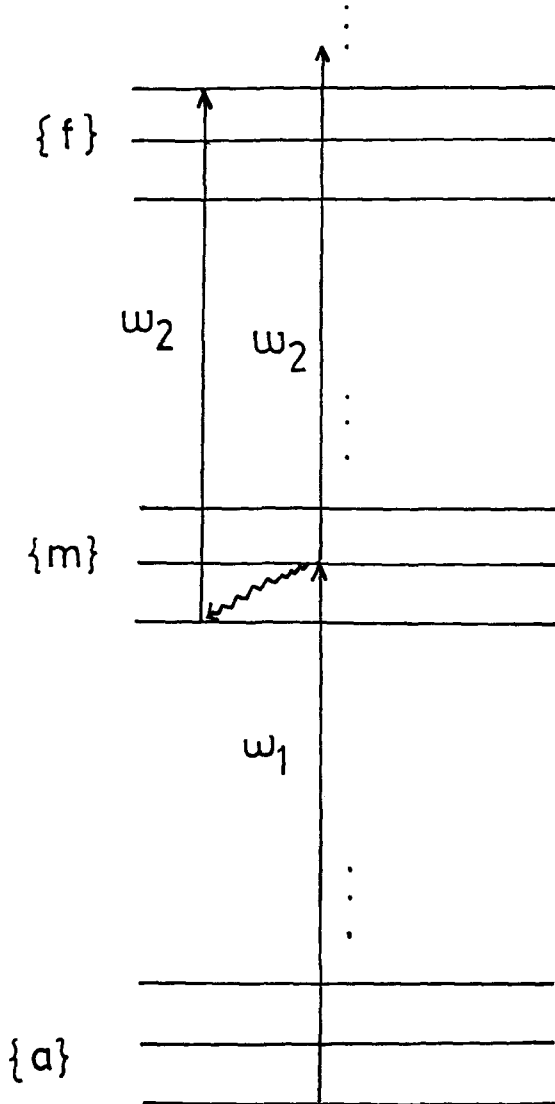


Fig. 3.1

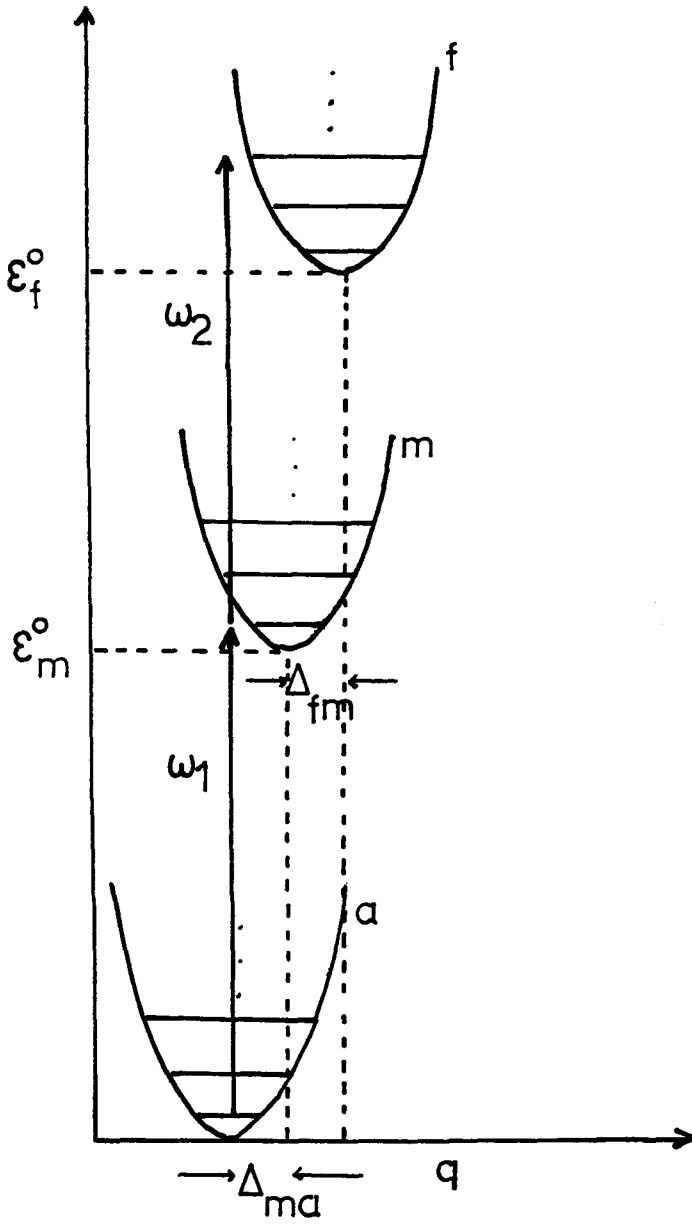


Fig. 3.2

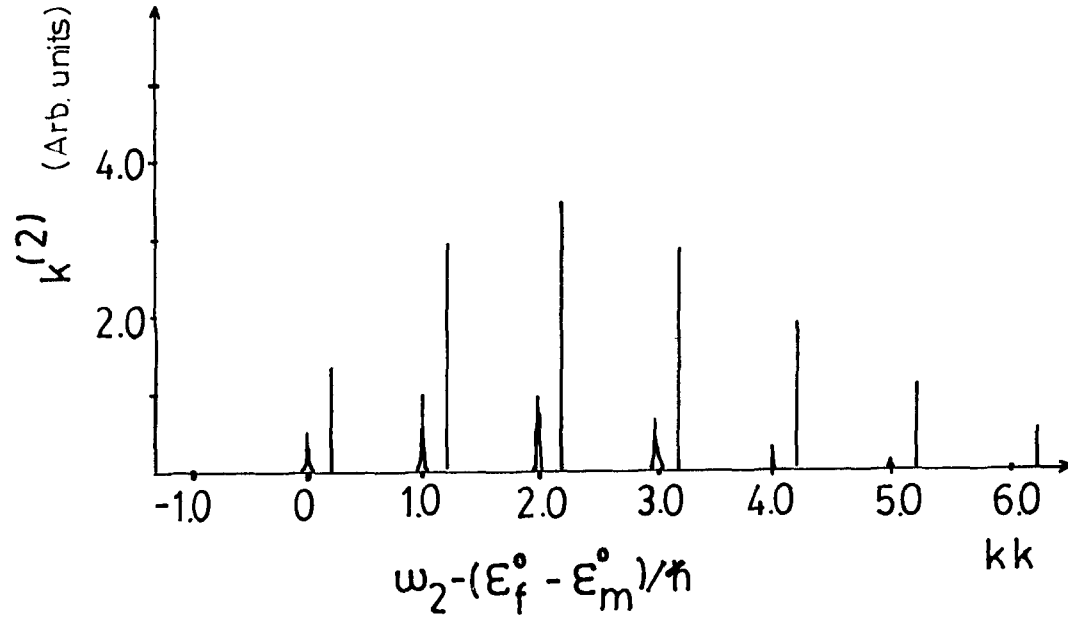


Fig. 3.3

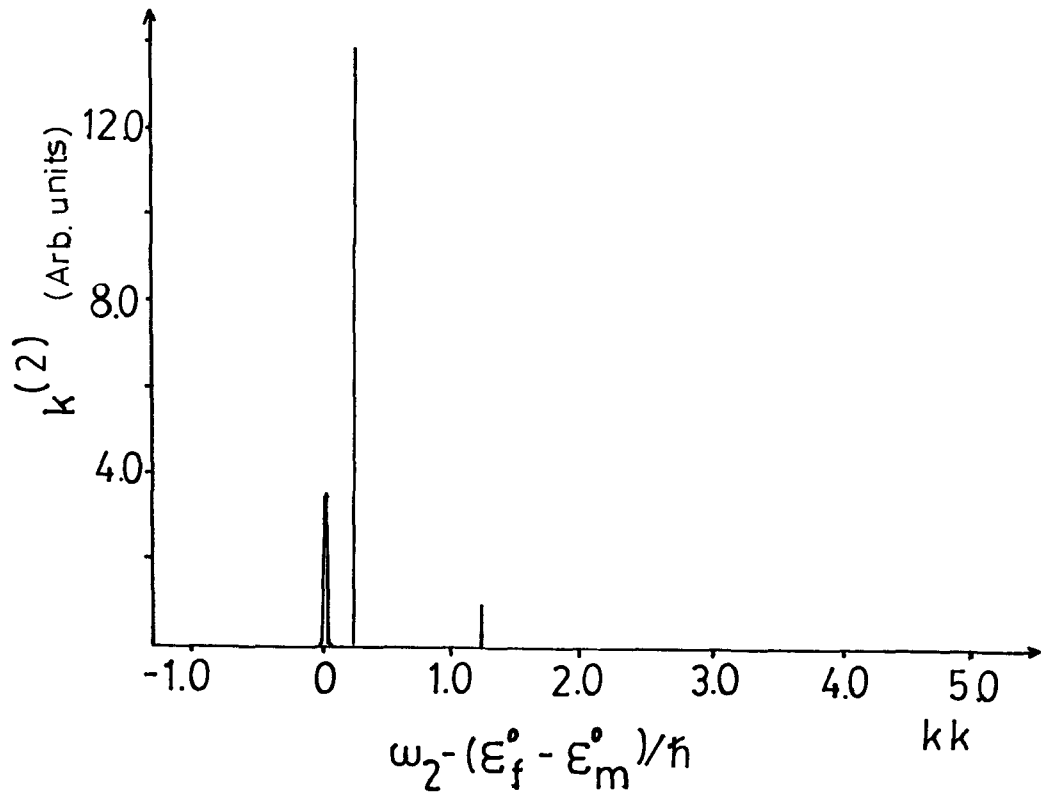


Fig. 3.4

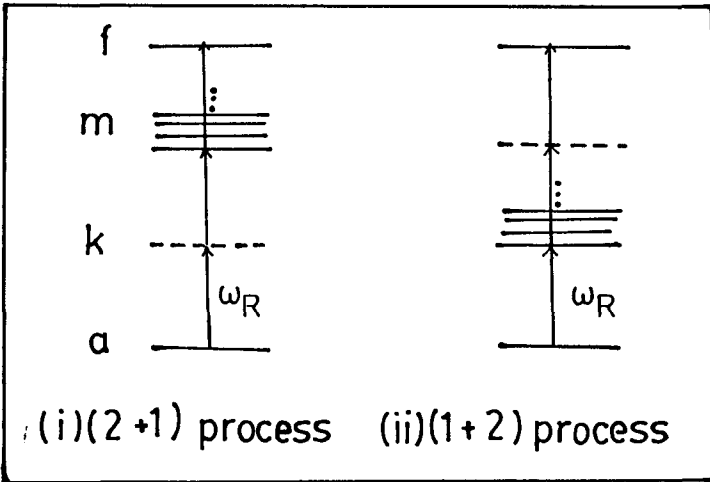


Fig. 3.5

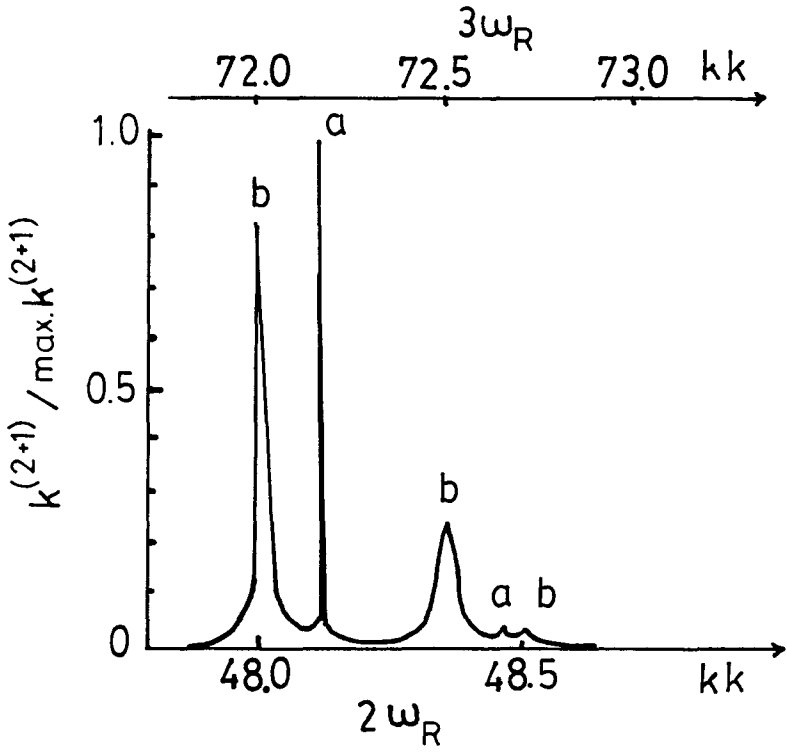


Fig. 3.6

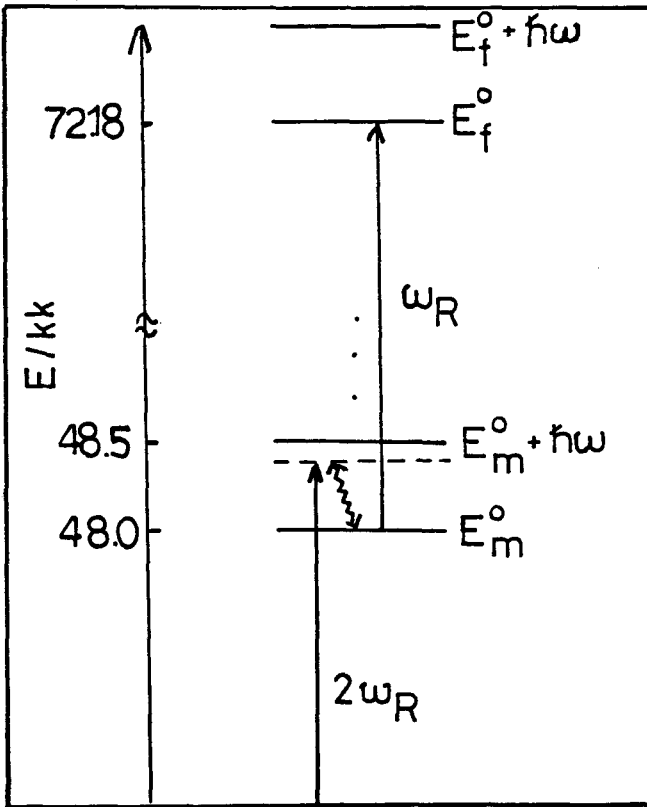


Fig. 3.7

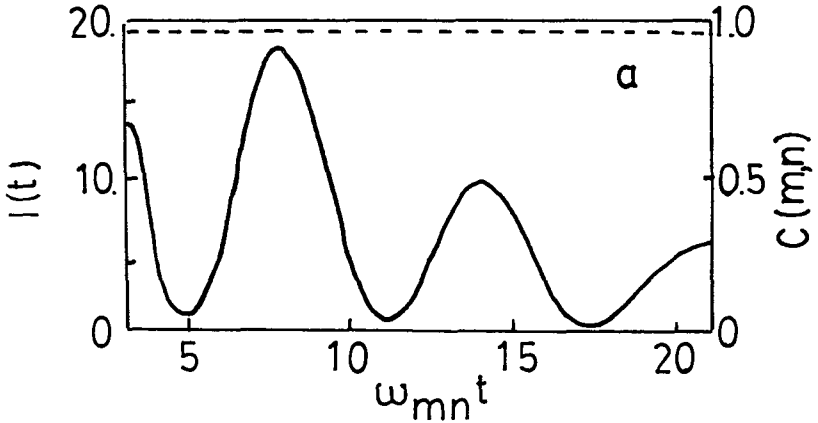


Fig. 3.8a

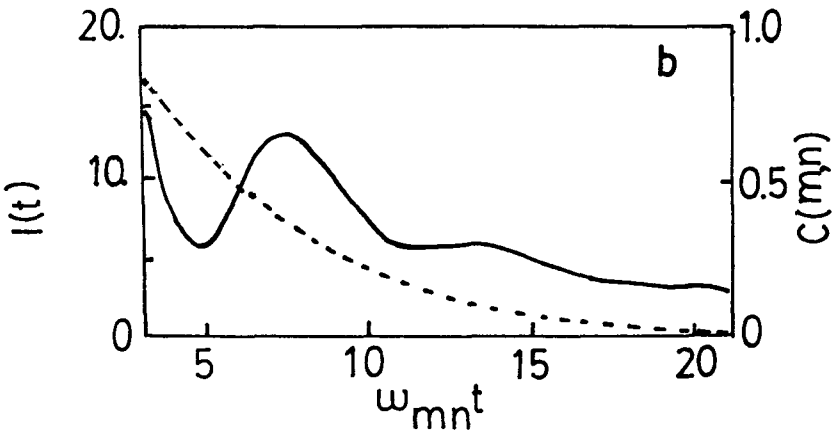


Fig. 3.8b

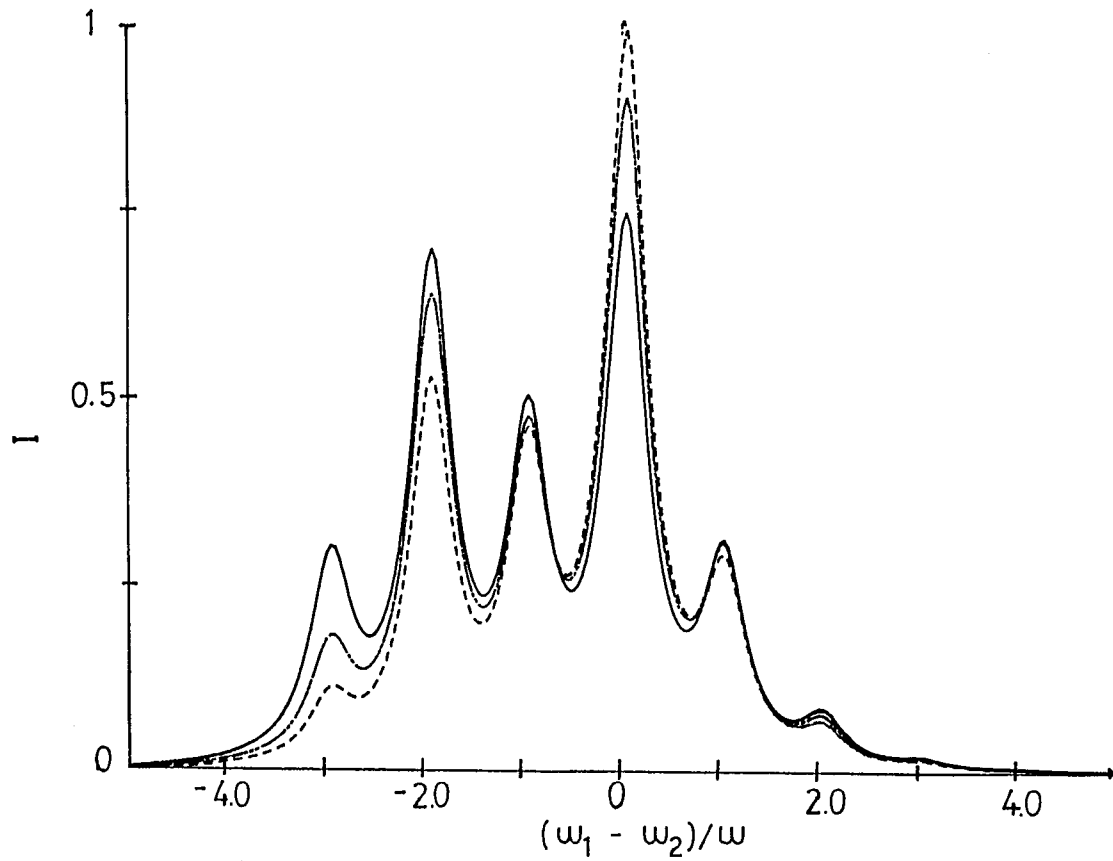


Fig. 3.9