

## Second Order Optical Process of A Randomly Modulated Multi-Level Atom\*

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A stochastic model of a multi-level atom interacting with its environment randomly in its excited states is considered. Assuming a two state-jump model for the random intermediate-state interaction, analytical expressions of emission spectra of three- and four-level atoms in the second order optical process are obtained. In each case, the expression is shown to be separated into three types of terms. Two types of terms correspond to the pure Raman spectrum and the luminescence, respectively, while the other type of term bears a mixed character contributing to broadening of the Raman line when the random modulation is slow and merging into the luminescence when the modulation is fast. This characteristic behavior is discussed with the use of the analytical expressions.

### §1. Introduction

Raman scattering and luminescence are both second order optical processes and have been a subject of active studies for a long time. The interaction of the system with its environment present in the intermediate states is called an *intermediate state interaction* (IMSI). In Raman scattering, the quantum coherence is conserved, whereas it is interrupted in luminescence by IMSI. Thus, a simple three-level atom gives only Raman scattering if the natural radiative damping is the only mechanism acting in the excited states. Luminescence appears when IMSI destructs the quantum phase coherence in the excited state.<sup>1-10)</sup> One of the present authors (R.K.) and his collaborators<sup>11-16)</sup> have extensively studied various stochastic models, where the perturbation from the environment (reservoir) is regarded as a stochastic Markovian process, for the purpose of understanding the nature of IMSI in the second order optical process. Since the stochastic approach does not rely upon perturbative calculations, it is particularly useful to see how the coherent and non-coherent parts are dependent on the relevant parameters of the problem changing from one extreme to another. However, the results are

usually still so much complicated that analytical expressions are not very transparent even if they are available and one has to appeal to numerical treatments in order to get physical understanding.

The present paper reports an analysis of three-level and four-level atoms modulated by the simplest two-state jump perturbation which allows straightforward algebraic treatments. This problem was treated by Takagawara<sup>17)</sup> some years ago, but his expression of the emission spectra was complicated and he showed only some numerical examples. We found that the analytical expressions can be separated into a few terms which correspond to different processes with different character of coherence. Although we have not been able to discover the general principle of separation, the achieved separation is by itself very interesting and seems to throw a light into the question of coherence of the second order optical process.

This paper is organized in the following way. The next section is a brief summary of the stochastic theory of IMSI in the second order optical process. In §3, we calculate the spectrum for a three-level atom with a diagonal modulation and discuss its features. In §4, the spectrum for a four-level atom with an off-diagonal modulation is calculated and discussed for three different models. The last section is devoted to the summary and conclu-

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sion.

## §2. Formulation

A formulation of IMSI in second order optical processes in the stochastic approach has been given by one of the present authors (R.K.) and his collaborators.<sup>11-16)</sup> In this section, we present a derivation of the expression for emission spectra following the formulation recently described by one of the authors (R.K.) in a conference report.<sup>18)</sup> A formula for the total emission intensity is also given.

We consider an atomic system  $S$  interacting with a radiation field  $\Phi$  and a reservoir  $R$ . The system  $S$  has three groups of quantum states, namely the initial state  $A$ , the intermediate state  $B_1, B_2, \dots$  and the final state  $C$ . Concerning the photon field  $\Phi$ , the frequency of incident light is denoted by  $\nu_1$  and that of emitted light by  $\nu_2$ . In the second order process, the atom in the state  $A$  absorbs a photon  $\nu_1$ , transfers to one of the intermediate states which are perturbed by the intermediate state interaction (if there are more than one such states), and then transfers from the same or other state to the final state  $C$  emitting a photon  $\nu_2$ . We ignore the nonresonant process in which the atom transfers to an intermediate state emitting a photon  $\nu_2$  before absorbing a photon  $\nu_1$ . Therefore, the energies of the initial, intermediate and the final states of the system  $S + \Phi$  are represented by

$$a = A + \nu_1, b_i = B_i \quad \text{and} \quad c = C + \nu_2, \quad (2.1)$$

where we put  $\hbar = 1$ . The interaction of  $S$  with the incident light is denoted by  $V_1$  and that with the emitted one by  $V_2$ . For simplicity we assume that the system  $S + \Phi$  interacts with its reservoir  $R$  only in the intermediate states. The IMSI is denoted by the Hamiltonian  $H_I$ . Thus, the Hamiltonian of the total system is written as

$$H_{\text{tot}} = H_{S+\Phi} + H_R + H_I + V_1 + V_2, \quad (2.2)$$

when  $S$  is in  $B$ 's, and

$$H_{\text{tot}} = H_{S+\Phi} + H_R + V_1 + V_2, \quad (2.3)$$

when  $S$  is in  $A$  or  $C$ . Here,  $H_{S+\Phi}$  and  $H_R$  denote the Hamiltonians of  $S + \Phi$  and  $R$  without interaction, respectively.

The density matrix for the total system

evolves in time following the equation

$$\dot{\rho}(t) = -i[H_{\text{tot}}, \rho(t)] \equiv -iH_{\text{tot}}^\times \rho(t), \quad (2.4)$$

where we have introduced the notation

$$O^\times X \equiv [O, X], \quad (2.5)$$

for a hyperoperator  $O^\times$ .

We assume the initial condition for eq. (2.4) as

$$\rho(0) = |a\rangle\langle a| \rho_R^0, \quad (2.6)$$

where  $\rho_R^0$  is the equilibrium density matrix of the reservoir  $R$  satisfying

$$H_R^\times \rho_R^0 = 0. \quad (2.7)$$

In a stochastic approach, the dynamical evolution of the reservoir  $R$  is replaced by a stochastic evolution. Let  $r$  denote a state of  $R$  and  $P_r(t)$  the probability for finding  $R$  in the state  $r$  at time  $t$ . The stochastic evolution of  $P_r(t)$  is assumed to follow the Markovian equation

$$\dot{P}_r(t) = -\sum_{r'} \Gamma(r, r') P_{r'}(t). \quad (2.8)$$

Thus, the stochastic operator  $\Gamma$  plays the role of  $iH_R^\times$  in the foregoing treatment. The IMSI is represented by the interaction Hamiltonian  $H_I(r)$  acting on  $S$  in the intermediate states when  $R$  is in the state  $r$ . The diagonal part of  $H_I(r)$  is the adiabatic random modulation for each of the intermediate states. In addition to this, there may be off-diagonal (nonadiabatic) modulations between the intermediate states. It has been shown many years ago by one of the authors (R.K.)<sup>19)</sup> that the evolution eq. (2.4) is replaced by

$$\dot{\rho}(t) = -i(H^\times(r) + V_1^\times + V_2^\times)\rho(t) - \Gamma\rho(t), \quad (2.9)$$

where  $H(r)$  is given by

$$H(r) = H_{S+\Phi} + H_I(r), \quad (2.10)$$

when  $S$  is in the intermediate states, and

$$H(r) = H_{S+\Phi}, \quad (2.11)$$

when  $S$  is in  $A$  or  $C$ . In eq. (2.9), the density matrix  $\rho(t)$  is considered as a vector in the space of reservoir states. The component  $\rho_r(t)$  is the density matrix of the system  $S + \Phi$ , averaged over all possible paths of evolution of the reservoir  $R$  specified to reach the state  $r$  at time  $t$ . The stochastic operator  $\Gamma$  operates

on this vector, while the hyper-operators operate on each component of the vector. Hereafter, we denote a quantum state of  $S + \Phi$  by a bra or a ket such as  $|a\rangle$ ,  $|b_i\rangle$  and  $|c\rangle$  or  $\langle a|$ ,  $\langle b_i|$  and  $\langle c|$ . Similarly state vectors of the reservoir are represented by round bras and kets such as  $(r|$ ,  $|r)$ ,  $(P|$  or  $|P)$ . In this notation

$$\Gamma(r, r') \equiv (r|\Gamma|r'), \quad (2.12)$$

in (2.8) and  $P_r(t) \equiv (r|P(t))$ . The equilibrium state of R is written as  $|0\rangle$  or  $\langle 0|$  and satisfies

$$\Gamma|0\rangle = 0 \quad \text{and} \quad \langle 0|\Gamma = 0 \quad (2.13)$$

with the normalization

$$\langle 0|0\rangle = 1. \quad (2.14)$$

Then the initial condition (2.6) is written as

$$\rho(0) = |a\rangle\langle a| \cdot |0\rangle. \quad (2.15)$$

By solving eq. (2.9) with this initial condition, we obtain a transition probability  $P(c, t)$  that the system has reached the final state  $c$  by the time  $t$  starting from the initial state  $a$ . This is given by

$$P(c, t) = \langle 0|\langle c|\rho(t)|c\rangle. \quad (2.16)$$

Per unit time, the rate of emission (photon counting rate)  $W(c, t)$  is given by

$$W(c, t) = dP(c, t)/dt. \quad (2.17)$$

Introducing the Laplace transforms of  $P(c, t)$  and  $W(c, t)$  by

$$P[c, s] = \int_0^\infty dt e^{-st} P(c, t), \quad (2.18)$$

and

$$W[c, s] = \int_0^\infty dt e^{-st} W(c, t) = sP[c, s]. \quad (2.19)$$

We write the continuous wave (CW) response as

$$W(c, \infty) = \lim_{t \rightarrow \infty} W(c, t) = \lim_{s \rightarrow 0} sW[c, s]. \quad (2.20)$$

The total intensity of emission integrated over all values of  $c$  is calculated as

$$I = \int_{-\infty}^\infty dc W(c, \infty). \quad (2.21)$$

Based on eqs. (2.15)–(2.17), we can calculate the CW response in the second order optical process. We expand the formal solution of eq. (2.9) to the second order of  $V_2$ :

$$\rho_2(t) = \int_0^t dt' \int_0^{t'} dt'' e^{-i(t-t')(H_{SR}^\times + V_1^\times)} (-iV_2^\times) e^{-i(t'-t'')(H_{SR}^\times + V_1^\times)} (-iV_2^\times) e^{-it''(H_{SR}^\times + V_1^\times)} \rho(0), \quad (2.22)$$

where

$$iH_{SR}^\times \equiv iH(r)^\times + \Gamma. \quad (2.23)$$

From eq. (2.16), the transition probability is given by

$$P(c, t) = \int_0^t dt_2 \int_0^{t_2} dt_1 \langle 0|\langle c|[e^{-i(t-t_2)(H_{SR}^\times + V_1^\times)} V_2 e^{-i(t_2-t_1)(H_{SR}^\times + V_1^\times)} \{e^{-it_1(H_{SR}^\times + V_1^\times)} \rho(0)\} V_2] |c\rangle |0\rangle + e^{-i(t-t_2)(H_{SR}^\times + V_1^\times)} \{e^{-i(t_2-t_1)(H_{SR}^\times + V_1^\times)} V_2 e^{-it_1(H_{SR}^\times + V_1^\times)} \rho(0)\} V_2] |c\rangle |0\rangle. \quad (2.24)$$

The photon counting rate can be written as

$$W(c, t) = \int_0^t dt' \langle 0|\langle c|V_2 e^{-i(t-t')(H-c-i\Gamma+V_1)} e^{-it'(H_{SR}^\times + V_1^\times)} \rho(0) V_2] |c\rangle |0\rangle + \text{c.c.} \quad (2.25)$$

Then the CW response, eq. (2.20), is formally given by

$$W(c, \infty) = \lim_{s \rightarrow 0} \langle 0|\langle c|V_2 \frac{1}{s + i(H-c) + \Gamma + iV_1} \rho^e V_2] |c\rangle |0\rangle + \text{c.c.}, \quad (2.26)$$

where

$$\rho^e = \lim_{s \rightarrow 0} \frac{s}{s + i(H_{SR}^\times + V_1^\times)} \rho(0), \quad (2.27)$$

represents the equilibrium-density operator in the presence of  $V_1$ .

We further expand eq. (2.26) to the second order in  $V_1$ . First we expand  $\rho^e$ . The zeroth order term does not contribute to eq. (2.26). The first and second order terms are given by

$$\rho_1^e = \lim_{s \rightarrow 0} \frac{1}{s + iH_{SR}^\times} (-iV_1^\times) \frac{s}{s + iH_{SR}^\times} \rho(0) = \lim_{s \rightarrow 0} \frac{1}{s + iH_{SR}^\times} \rho(0) iV_1 + \dots, \tag{2.28}$$

$$\begin{aligned} \rho_2^e &= \lim_{s \rightarrow 0} \frac{1}{s + iH_{SR}^\times} (-iV_1^\times) \frac{1}{s + iH_{SR}^\times} (-iV_1^\times) \frac{s}{s + iH_{SR}^\times} \rho(0) \\ &= \lim_{s \rightarrow 0} \frac{1}{s + iH_{SR}^\times} \left[ \left\{ \frac{1}{s + iH^\times + \Gamma} V_1 \rho(0) \right\} V_1 + V_1 \left\{ \frac{1}{s + iH^\times + \Gamma} \rho(0) V_1 \right\} \right], \end{aligned} \tag{2.29}$$

with the use of  $H_{SR}^\times \rho(0) = 0$ , where the irrelevant terms are omitted. The first order term eq. (2.28) has the matrix elements  $\langle a | \rho_1^e | b_n \rangle$ , while  $\rho_2^e$  has elements only between the intermediate states. Next, we expand the first propagator in eq. (2.26) of right hand side in  $V_1$ . The zeroth order term combines with  $\rho_2^e$  and the first order term with  $\rho_1^e$ . The final expression is given by<sup>18)</sup>

$$\begin{aligned} W(c, \infty) &= \lim_{s \rightarrow 0} \left\{ \sum_{ij} \sum_{kl} \left[ \left( 0 \left| \langle c | V_2 | b_j \rangle \langle b_j | \frac{1}{s + \Gamma + \gamma_b + i(H - c)} | b_i \rangle \right. \right. \right. \\ &\quad \times \langle b_i | V_1 | a \rangle \frac{1}{s + \Gamma + i(a - c)} \langle c | V_2 | b_l \rangle^* \\ &\quad \left. \left. \left. \times \langle b_l | \frac{1}{s + \Gamma + \gamma_b + i(H - a)} | b_k \rangle^* \langle b_k | V_1 | a \rangle^* \right| 0 \right) \right] \right\} \end{aligned} \tag{2.30.I}$$

$$\begin{aligned} &+ \sum_{ij} \sum_{kl} \sum_{nm} \left( 0 \left| \langle c | V_2 | b_n \rangle \langle b_n | \frac{1}{s + \Gamma + \gamma_b + i(H - c)} | b_l \rangle \right. \right. \\ &\quad \times \langle b_l b_m | \frac{1}{s + \Gamma + 2\gamma_b + iH^\times} | b_j b_k \rangle \langle a | V_1 | b_k \rangle \\ &\quad \times \langle b_j | \frac{1}{s + \Gamma + \gamma_b + i(H - a)} | b_i \rangle \langle b_i | V_1 | a \rangle \left| 0 \right) \langle b_m | V_2 | c \rangle \end{aligned} \tag{2.30.II}$$

$$\begin{aligned} &+ \sum_{ij} \sum_{kl} \sum_{mn} \left( 0 \left| \langle c | V_2 | b_n \rangle \langle b_n | \frac{1}{s + \Gamma + \gamma_b + i(H - c)} | b_l \rangle \right. \right. \\ &\quad \times \langle b_l b_m | \frac{1}{s + \Gamma + 2\gamma_b + iH^\times} | b_k b_j \rangle \langle b_k | V_1 | a \rangle \\ &\quad \times \langle b_j | \frac{1}{s + \Gamma + \gamma_b + i(H - a)} | b_i \rangle^* \langle b_i | V_1 | a \rangle^* \\ &\quad \left. \left. \left. \times \langle b_m | V_2 | c \rangle \right| 0 \right) \right\} + \text{c.c.} \end{aligned} \tag{2.30.III}$$

Here, we have introduced the notation

$$\langle b_i b_j | A | b_k b_l \rangle = \langle b_i | \{ A | b_k \} \langle b_l | | b_j \rangle \tag{2.31}$$

for a hyperoperator  $A$  operating on  $|b_k\rangle\langle b_l|$ . In eq. (2.30), it is assumed that the natural radiation damping of the intermediate states is given by a phenomenological damping constant  $\gamma_b$  for the states  $B$ 's. As we shall see in later sections, eq. (2.30.I) comes from  $\rho_1^e$  and gives rise to the Raman and broadened Raman parts, whereas eqs. (2.30.II) and (2.30.III) are due to  $\rho_2^e$  and gives the luminescence part and at the same time compensates the negative contributions from  $\rho_1^e$ .

The total intensity of emission, eq. (2.21), can also be calculated as

$$\begin{aligned}
I &= \int_{-\infty}^{\infty} dc \left( 0 \left| \langle c | V_2 \frac{1}{i(H-c) + \Gamma + iV_1} \rho^e V_2 | c \rangle \right| 0 \right) + \text{c.c.} \\
&= 2\pi \sum_{ij} \sum_{kmn} \left( 0 \left| \langle c | V_2 | b_n \rangle \langle b_n b_m | \frac{1}{\Gamma + 2\gamma_b + iH^\times} | b_j b_k \rangle \left\{ \langle b_j | \frac{1}{\Gamma + \gamma_b + i(H-a)} | b_i \rangle \langle b_i | V_1 | a \rangle \right| 0 \right) \right. \\
&\quad \left. \times \langle b_k | V_1 | a \rangle^* \langle b_m | V_2 | c \rangle + \langle b_k | \frac{1}{\Gamma + \gamma_b + i(H-a)} | b_i \rangle^* \langle b_j | V_1 | a \rangle \right| 0 \rangle \langle b_i | V_1 | a \rangle^* \langle b_m | V_2 | c \rangle \left. \right\}.
\end{aligned} \tag{2.32}$$

### §3. Three-Level Atom with Diagonal Modulation

In this section, we consider a three-level atom with a random adiabatic modulation  $\Omega$  which shifts the level of the intermediate state  $B$ . Then, the IMSI Hamiltonian (eqs. (2.10) and (2.11)) is written as

$$H(\Omega) = \begin{bmatrix} a & 0 & 0 \\ 0 & b + \Omega & 0 \\ 0 & 0 & c \end{bmatrix}. \tag{3.1}$$

The modulation  $\Omega$  is further assumed to take only two values  $\Omega = \pm \Delta$  randomly with the average jumping rate  $\gamma_m = 1/\tau_m$  (see Fig. 1). This is called a *two-state jump model*. The modulation  $\Omega$  is expressed in a matrix form as

$$\Omega = \begin{pmatrix} \Delta & 0 \\ 0 & -\Delta \end{pmatrix}, \tag{3.2}$$

in the space of the two states. The time evolu-

tion of the random modulation is described by the operator

$$\Gamma = \frac{\gamma_m}{2} \begin{pmatrix} 1 & -1 \\ -1 & 1 \end{pmatrix}. \tag{3.3}$$

The eigenvectors of  $\Gamma$  corresponding to the equilibrium state are given by

$$|0\rangle = \frac{1}{2} \begin{pmatrix} 1 \\ 1 \end{pmatrix} \quad \text{and} \quad \langle 0| = (1, 1), \tag{3.4}$$

and other eigenvectors are

$$|1\rangle = \frac{1}{2} \begin{pmatrix} 1 \\ -1 \end{pmatrix} \quad \text{and} \quad \langle 1| = (1, -1). \tag{3.5}$$

These eigenvectors satisfy the following relations:

$$\begin{aligned}
\langle 0 | \Omega | 0 \rangle &= \langle 1 | \Omega | 1 \rangle = 0, \\
\langle 0 | \Omega | 1 \rangle &= \langle 1 | \Omega | 0 \rangle = \Delta, \\
\langle 0 | \Gamma | 0 \rangle &= 0 \quad \text{and} \quad \langle 1 | \Gamma | 1 \rangle = \gamma_m.
\end{aligned} \tag{3.6}$$

By eq. (2.30), the spectrum  $W$  is expressed as<sup>17)</sup>

$$\begin{aligned}
W &= |\langle c | V_2 | b \rangle|^2 |\langle b | V_1 | a \rangle|^2 \\
&\quad \times \left\{ \lim_{s \rightarrow 0} \left( 0 \left| \frac{1}{\gamma_b + \Gamma - i(\omega_2 - \Omega)} \right| 0 \right) \frac{1}{s + i(\omega_1 - \omega_2)} \left( 0 \left| \frac{1}{\gamma_b + \Gamma + i(\omega_1 - \Omega)} \right| 0 \right) \right. \\
&\quad + \left( 0 \left| \frac{1}{\gamma_b + \Gamma - i(\omega_2 - \Omega)} \right| 1 \right) \frac{1}{\gamma_m + i(\omega_1 - \omega_2)} \left( 1 \left| \frac{1}{\gamma_b + \Gamma + i(\omega_1 - \Omega)} \right| 0 \right) \\
&\quad + \left( 0 \left| \frac{1}{\gamma_b + \Gamma - i(\omega_2 - \Omega)} \right| 0 \right) \frac{1}{2\gamma_b} \left[ \left( 0 \left| \frac{1}{\gamma_b + \Gamma + i(\omega_1 - \Omega)} \right| 0 \right) + \text{c.c.} \right] \\
&\quad \left. + \left( 0 \left| \frac{1}{\gamma_b + \Gamma - i(\omega_2 - \Omega)} \right| 1 \right) \frac{1}{2\gamma_b + \gamma_m} \left[ \left( 1 \left| \frac{1}{\gamma_b + \Gamma + i(\omega_1 - \Omega)} \right| 0 \right) + \text{c.c.} \right] \right\} + \text{c.c.},
\end{aligned} \tag{3.7}$$

where

$$\omega_1 = a - b \quad \text{and} \quad \omega_2 = c - b \tag{3.8}$$

are the off-resonance frequencies of the incident and the emitted radiation.

The spectrum  $W$  can be rearranged into a sum of three terms as (see also Appendix)

$$W = W_R + W_{BR} + W_L, \tag{3.9}$$

with

$$W_R = |\langle c | V_2 | b \rangle|^2 |\langle b | V_1 | a \rangle|^2 2\pi \cdot \delta(\omega_1 - \omega_2) \frac{1}{(\gamma_b + \gamma(\omega_1))^2 + (\omega_1 - \delta(\omega_1))^2}, \tag{3.10}$$

$$W_{BR} = |\langle c | V_2 | b \rangle|^2 |\langle b | V_1 | a \rangle|^2 2 \frac{\gamma_m}{\gamma_m^2 + (\omega_1 - \omega_2)^2} \cdot \frac{1}{(\gamma_b + \gamma_m)^2 + \omega_1^2} \cdot \frac{1}{(\gamma_b + \gamma_m)^2 + \omega_2^2} \\ \times \frac{\Delta^2 \{ [-\omega_1 \cdot \omega_2 + (\gamma_b + \gamma_m)^2 + \Delta^2]^2 + (\gamma_b + \gamma_m)^2 \cdot (\omega_1 + \omega_2)^2 \}}{[(\gamma_b + \gamma(\omega_1))^2 + (\omega_1 - \delta(\omega_1))^2][(\gamma_b + \gamma(\omega_2))^2 + (\omega_2 - \delta(\omega_2))^2]}, \tag{3.11}$$

and

$$W_L = 2 \mathfrak{W}_{ab}^2 \frac{\gamma_b + \gamma_m}{\gamma_b \cdot \gamma_m} \mathfrak{W}_{bc}^2, \tag{3.12}$$

where

$$\mathfrak{W}_{ab}^2 = W_{a \rightarrow b}^a \cdot \frac{\gamma(\omega_1)}{\gamma_b + \gamma(\omega_1)} \cdot \frac{\gamma_m}{\gamma_b + \gamma_m}, \tag{3.13}$$

and

$$\mathfrak{W}_{bc}^2 = W_{b \rightarrow c}^e \cdot \frac{\gamma(\omega_2)}{\gamma_b + \gamma(\omega_2)} \cdot \frac{\gamma_m}{\gamma_b + \gamma_m}. \tag{3.14}$$

Here,

$$W_{a \rightarrow b}^a = |\langle b | V_1 | a \rangle|^2 \text{Re} \left( \left\langle 0 \left| \frac{1}{\gamma_b + \Gamma + i(\omega_1 - \Omega)} \right| 0 \right\rangle \right) = |\langle b | V_1 | a \rangle|^2 \cdot \frac{\gamma_b + \gamma(\omega_1)}{(\gamma_b + \gamma(\omega_1))^2 + (\omega_1 - \delta(\omega_1))^2}, \tag{3.15}$$

and

$$W_{b \rightarrow c}^e = |\langle c | V_2 | b \rangle|^2 \cdot \frac{\gamma_b + \gamma(\omega_2)}{(\gamma_b + \gamma(\omega_2))^2 + (\omega_2 - \delta(\omega_2))^2}, \tag{3.16}$$

are the rates of absorption and emission of photon respectively. In the above expressions

$$\gamma(\omega) = \frac{(\gamma_b + \gamma_m)\Delta^2}{(\gamma_b + \gamma_m)^2 + \omega^2} \quad \text{and} \quad \delta(\omega) = \frac{\omega\Delta^2}{(\gamma_b + \gamma_m)^2 + \omega^2}, \tag{3.17}$$

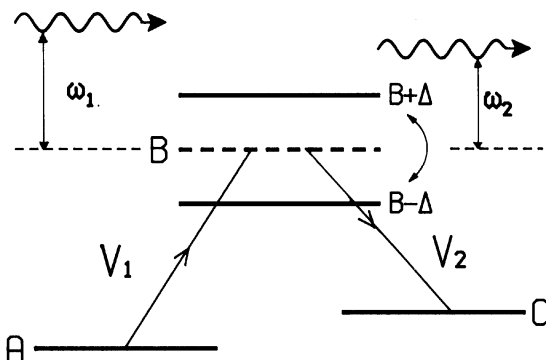


Fig. 1. A three-level atom with a diagonal modulation.

are the damping and the level shift induced by the random modulation. It is noticed that the factor  $\mathfrak{W}_{ab}^2$  and  $\mathfrak{W}_{bc}^2$  in eq. (3.12) are closely related to the absorption and the emission rates, eqs. (3.15) and (3.16).

The total intensity of emission is calculated from eq. (2.32) to be

$$I_{\text{tot}} = |\langle c | V_2 | b \rangle|^2 \times 2\pi W_{a \rightarrow b}^a / \gamma_b. \tag{3.18}$$

The first term of eq. (3.9), namely  $W_R$  given by eq. (3.10), comes from the real part of the expression  $(s + i(\omega_1 - \omega_2))^{-1}$  in the first line of the expression eq. (3.7) and represents a pure Raman process. It is a sharp spectral line of a

delta function type located at  $\omega_1 = \omega_2$  with the intensity in a resonance form in which the damping and the resonance frequency are modified by the random diagonal perturbation. Its ratio to the total intensity of emission is

$$I_R/I_{\text{tot}} = \int W_R d\omega_2 / I_{\text{tot}} = \gamma_b / \{\gamma_b + \gamma(\omega_1)\}. \quad (3.19)$$

The second term, namely  $W_{\text{BR}}$  given by eq. (3.11), is the contribution by the second line of eq. (3.7) and is called here the broadened Raman term because of the presence of the factor  $\gamma_m / [\gamma_m^2 + (\omega_1 - \omega_2)^2]$ . This may be interpreted as the broadening of the initial and the final states of the composite system S+R. Although we assume the reservoir R to be decoupled from the system S in these states, the coupling existent in the intermediate states allows exchange of energy for the reservoir through the optical process. When the modulation is slow, namely when  $\gamma_m$  is small, this gives a broadened Raman-like line at the Raman position of the emission spectrum. When the modulation becomes faster, however, the spectrum bears the nature of

luminescence as we discuss later in more details. In this sense the terminology is not quite proper, but we use it hereafter since we find no better word.

The third term is purely luminescence. It consists of two distinct factors corresponding to absorption of an incident photon and emission of a luminescence photon. This sort of structure will be more apparent in the case of a four level system as we shall see later. A delicate point is that these factors  $\mathcal{W}_{\text{ab}}$  and  $\mathcal{W}_{\text{bc}}$  are not identical with the absorption and the emission rates  $W_{\text{a} \rightarrow \text{b}}^{\text{a}}$  and  $W_{\text{b} \rightarrow \text{c}}^{\text{c}}$ . The reason for this is that  $W_{\text{L}}$  is not the whole of luminescence, which is partly contributed also by  $W_{\text{BR}}$  as will be seen later.

We now discuss how the change of the modulation rate  $\gamma_m$  affects the nature and the relative importance of these terms.

### 3.1 Very slow modulation case

If the modulation rate  $\gamma_m$  is equal to zero, or it is smaller than any of other parameters, only the pure Raman process should appear. This is contributed by  $W_{\text{R}}$  and  $W_{\text{BR}}$ , because the latter becomes

$$W_{\text{BR}} = |\langle c | V_2 | b \rangle|^2 |\langle b | V_1 | a \rangle|^2 2\pi \cdot \delta(\omega_1 - \omega_2) \cdot \frac{\Delta^2}{[\gamma_b^2 + (\omega_1 + \Delta)^2][\gamma_b^2 + (\omega_1 - \Delta)^2]}, \quad (3.20)$$

which is combined with  $W_{\text{R}}$  to result in

$$W = W_{\text{R}} + W_{\text{BR}} = |\langle c | V_2 | b \rangle|^2 |\langle b | V_1 | a \rangle|^2 2\pi \cdot \delta(\omega_1 - \omega_2) \frac{1}{2} \left( \frac{1}{\gamma_b^2 + (\omega_1 + \Delta)^2} + \frac{1}{\gamma_b^2 + (\omega_1 - \Delta)^2} \right). \quad (3.21)$$

This is the averaged spectrum of two pure Raman processes through the intermediate states  $B + \Delta$  and  $B - \Delta$ . When the modulation rate is finite, the Raman line is a superposition of a delta-type peak of  $W_{\text{R}}$  eq. (3.10) and a Lorentzian peak contributed by the term  $W_{\text{BR}}$ . The wing of the latter extends to the frequencies  $\omega_2 = \pm \Delta$ , which correspond to the luminescence emission, where the intensity is enhanced by the resonance factor in the denominator to form peaks when  $\gamma_m$  is sufficiently large. These peaks are indistinguishable from the luminescence coming from the term  $W_{\text{L}}$ , but are rather minor parts of the whole spectrum as long as  $\gamma_m$  is not too

large, namely  $\gamma_m < \Delta^2 / \gamma_b$  (see eqs. (3.25) and (3.26)). The resultant luminescence spectrum has two peaks at  $\omega_2 = \pm \Delta$ , when  $\gamma_m$  is not too large, but they are narrowed to a single peak at  $\omega_2 = 0$  when  $\gamma_m$  exceeds  $\Delta$ .

### 3.2 Fast modulation case

In random frequency modulation problems, the modulation effect is said motionally narrow when the condition

$$\Delta / \gamma_m \ll 1 \quad (3.22)$$

is satisfied between the rate of modulation and the magnitude of modulation. Then it produces an additional exponential decay rate

$$\gamma' = \Delta^2 / \gamma_m \tag{3.23}$$

for the phase memory, which causes a transverse decay of the excited state superposed onto the natural damping. In the present problem, the situation is a little more complicated because the effect is dependent on other parameters of the problem, namely the

natural damping constant  $\gamma_b$  and the off-resonance  $\omega_1$ . If the modulation rate  $\gamma_m$  is larger than these parameters, the additional transverse relaxation produces a partial destruction of dynamical coherence and results in luminescence. In this situation the whole spectrum is represented by

$$W = |\langle c | V_2 | b \rangle|^2 |\langle b | V_1 | a \rangle|^2 \left( 2\pi \cdot \delta(\omega_1 - \omega_2) \frac{1}{(\gamma_b + \gamma')^2 + \omega_1^2} + 2 \frac{\gamma_b + \gamma'}{(\gamma_b + \gamma')^2 + \omega_1^2} \cdot \frac{\gamma'}{\gamma_b(\gamma_b + \gamma')} \cdot \frac{\gamma_b + \gamma'}{(\gamma_b + \gamma')^2 + \omega_2^2} \right). \tag{3.24}$$

The first term is the pure Raman effect coming from the term  $W_R$  while the second term is the luminescence. The latter is the resultant of the terms  $W_L$  and  $W_{BR}$  in eq. (3.9). We find that

$$W_{BR} = 2W'_{a \rightarrow b} \cdot \frac{\gamma'}{\gamma_b + \gamma'} \cdot \frac{1}{\gamma_b} \cdot \frac{\gamma_b}{\gamma_b + \gamma'} \cdot W'_{b \rightarrow c}, \tag{3.25}$$

$$W_L = 2W'_{a \rightarrow b} \cdot \frac{\gamma'^2}{(\gamma_b + \gamma')^2} \cdot \frac{1}{\gamma_b} \cdot W'_{b \rightarrow c}, \tag{3.26}$$

and

$$W_{BR} + W_L = 2W'_{a \rightarrow b} \cdot \frac{\gamma'}{\gamma_b(\gamma_b + \gamma')} \cdot W'_{b \rightarrow c}. \tag{3.27}$$

Here,

$$W'_{a \rightarrow b} = |\langle a | V_1 | b \rangle|^2 \cdot \frac{\gamma_b + \gamma'}{(\gamma_b + \gamma')^2 + \omega_1^2}, \tag{3.28}$$

and

$$W'_{b \rightarrow c} = |\langle b | V_2 | c \rangle|^2 \cdot \frac{\gamma_b + \gamma'}{(\gamma_b + \gamma')^2 + \omega_2^2} \tag{3.29}$$

are the absorption and emission rates in this narrowing condition. In this case the resultant

luminescence has the form of product of two distinct processes of absorption and emission. The term  $W_{BR}$  becomes a part of incoherent luminescence process and contributes the fraction  $\gamma_b / (\gamma_b + \gamma')$  of the luminescence intensity. In this way the discrepancies between the factors  $\mathfrak{W}_{ab}$  and  $\mathfrak{W}_{bc}$  with  $W'_{a \rightarrow b}$  and  $W'_{b \rightarrow c}$  in the expression (3.12) of  $W_L$  are remedied by the contribution from the term  $W_{BR}$  in the motional narrowing limit. Figure 2 illustrates how the intensities are divided into respective terms in the narrowing limit.

As the modulation rate becomes so large that it holds

$$\gamma' \ll \gamma_b, \tag{3.30}$$

then the luminescence loses its intensity and the emission becomes purely coherent Raman scattering.

### 3.3 Strong off-resonance

Obviously, the second order scattering must be almost coherent Raman-like when the off resonance  $\omega_1$  is sufficiently large. This is easily

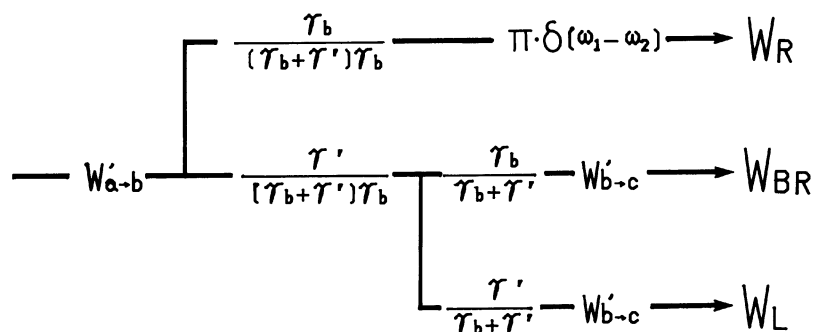


Fig. 2. Branching features of the spectral of three-level atom in the motional narrowing limit. The factors  $W'_{a \rightarrow b}$  and  $W'_{b \rightarrow c}$  are defined by eqs. (3.28) and (3.29).



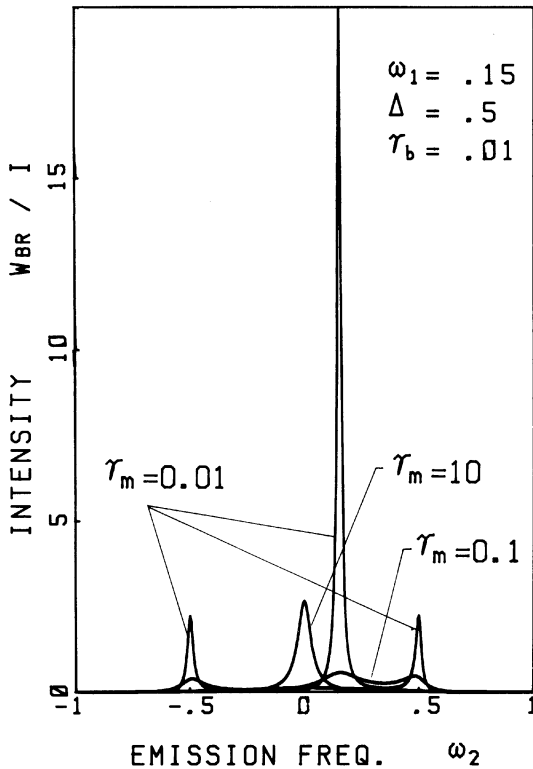


Fig. 3. Emission spectra of the broadened Raman term of a three level atom with a diagonal modulation.

seen from eq. (3.19). The ratio of coherent Raman intensity to the total intensity is close to one if the condition

$$I_R/I_{tot} = \gamma_b / (\gamma_b + \gamma(\omega_1)) \approx 1, \quad (3.31)$$

is satisfied. Therefore the luminescence should vanish when the off-resonance is so large that  $\gamma(\omega_1)$  is much smaller than  $\gamma_b$ .

Figures 3 and 4 illustrate the spectral distribution of  $W_{BR}$  and  $W_L$  normalized by the total intensity (3.18) for different values of  $\gamma_m$  fixing the other parameters as  $\omega_1=0.15$ ,  $\Delta=0.5$  and  $\gamma_b=0.01$ . In Fig. 3,  $W_{BR}$  is seen to have sharp peaks at the Raman position  $\omega_2=\omega_1$  and at the luminescence positions  $\omega_2=\pm\Delta$  already for the smallest value of  $\gamma_m$ , namely  $\gamma_m=0.01$ . The Raman peak declines rather quickly as  $\gamma_m$  increases. For  $\gamma_m=0.1$  it becomes almost unnoticeable. The luminescence peaks at  $\omega_2=\pm 0.5$  are distinct for small values of  $\gamma_m$ , but they merge into a single peak at the average position  $\omega_2=0$  for large values of  $\gamma_m$ , say 10. In Fig. 4, the luminescence intensity of  $W_L$  are seen to be considerably larger than that of  $W_{BR}$ . Peaks at  $\omega_2=\pm 0.5$  are distinct for  $\gamma_m=0.01$  and 0.1. The motional narrowing to a single peak at  $\omega_2=0$  is seen for  $\gamma_m=1$  and 10.

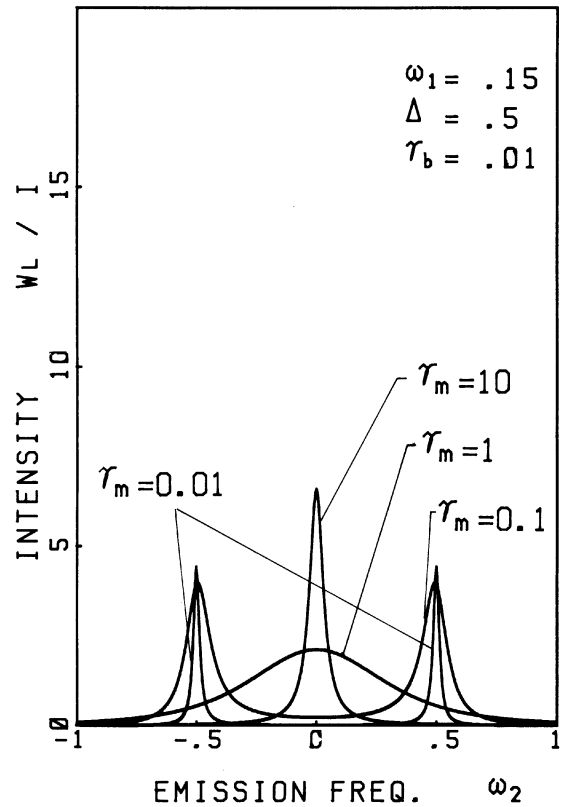


Fig. 4. Emission spectra of the luminescence term of three level atom with a diagonal modulation.

#### §4. Four-Level Atom with Off-Diagonal Modulation

Next we consider a four-level atom with the intermediate states  $B_1$  and  $B_2$ . The IMSI from the reservoir is assumed to give rise to an off-diagonal interaction between  $B_1$  and  $B_2$ . In this case, IMSI Hamiltonian is written as

$$H(\Omega) = \begin{bmatrix} a & 0 & 0 & 0 \\ 0 & b_1 & \Omega & 0 \\ 0 & \Omega & b_2 & 0 \\ 0 & 0 & 0 & c \end{bmatrix}. \quad (4.1)$$

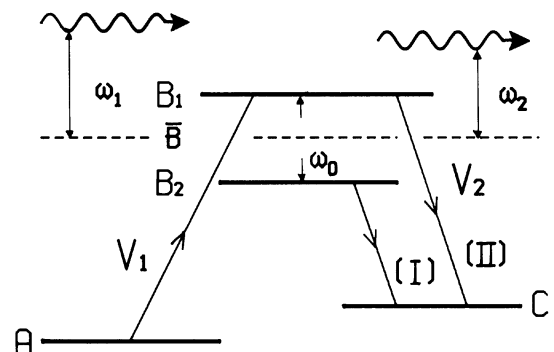


Fig. 5. A four-level atom with an off-diagonal modulation. The interaction  $V_1$  connects  $A$  and  $B_1$ . Three models are considered for  $V_2$  as follows:  $V_2$  connects  $C$  with  $B_2$  (I),  $B_1$  (II) and both  $B_1$  and  $B_2$  (I+II).



Here,

$$W_{a \rightarrow b1}^a = |\langle a | V_1 | b_1 \rangle|^2 \cdot \frac{\gamma_b + \gamma(\omega_{1+})}{(\gamma_b + \gamma(\omega_{1+}))^2 + (\omega_{1-} - \delta(\omega_{1+}))^2} \quad (4.11)$$

and

$$W_{b2 \rightarrow c}^e = |\langle b_2 | V_2 | c \rangle|^2 \cdot \frac{\gamma_b + \gamma(\omega_{2-})}{(\gamma_b + \gamma(\omega_{2-}))^2 + (\omega_{2+} - \delta(\omega_{2-}))^2}. \quad (4.12)$$

Here,  $\delta(\omega)$  and  $\gamma(\omega)$  are defined by eq. (3.17) and  $\gamma_{12}$  is given by

$$\gamma_{12} = \frac{(2\gamma_b + \gamma_m)\Delta^2}{(2\gamma_b + \gamma_m)^2 + \omega_0^2}. \quad (4.13)$$

The middle factor of eq. (4.8) coincides with the rate of transition from  $B_1$  to  $B_2$  caused by the perturbation  $\Omega$ , which is given by

$$W_{b1 \rightarrow b2} = \langle b_2 b_2 | \frac{1}{\Gamma + 2\gamma_b + iH^\times} | b_1 b_1 \rangle + \text{c.c.} = \frac{\gamma_{12}}{\gamma_b(\gamma_b + \gamma_{12})}. \quad (4.14)$$

For this model, the pure Raman process does not appear in general, because levels  $B_1$  and  $B_2$  are connected by the modulation  $\Omega$  which perturbs the coherence of the quantum evolution from the initial to the final states. This brings about a broadened Raman process which maintains a partial quantum coherence. Only in the static limit  $\gamma_m \rightarrow 0$ , this becomes a pure Raman effect, namely

$$W_{BR} = |\langle a | V_1 | b_1 \rangle|^2 |\langle b_2 | V_2 | c \rangle|^2 \times 2\pi \cdot \delta(\omega_1 - \omega_2) \frac{\Delta^2}{[\gamma_b^2 + (\omega_1 + \sqrt{\Delta^2 + \omega_0^2/4})^2][\gamma_b^2 + (\omega_1 - \sqrt{\Delta^2 + \omega_0^2/4})^2]}. \quad (4.15)$$

The right hand side of this equation has the resonance form corresponding to the eigenstates of the Hamiltonian (4.3) with a constant  $\Omega$ .

In the motional narrowing limit  $\gamma_m \gg \Delta$  with  $\Delta^2/\gamma_m = \gamma'$ , the quantum coherence in  $W_{BR}$  is completely disturbed by the modulation and  $W_{BR}$  takes the form

$$W_{BR} = 2W'_{a \rightarrow b1} \cdot \frac{\gamma'}{\gamma_b + \gamma'} \cdot \frac{1}{\gamma_b} \cdot \frac{\gamma_b}{\gamma_b + \gamma'} \cdot W'_{b2 \rightarrow c}. \quad (4.16)$$

Here,  $W'_{a \rightarrow b1}$  and  $W'_{b2 \rightarrow c}$  are the rates of absorption and emission expressed as

$$W'_{a \rightarrow b1} = |\langle a | V_1 | b_1 \rangle|^2 \cdot \frac{\gamma_b + \gamma'}{(\gamma_b + \gamma')^2 + \omega_{1-}^2} \quad (4.17)$$

and

$$W'_{b2 \rightarrow c} = |\langle b_2 | V_2 | c \rangle|^2 \cdot \frac{\gamma_b + \gamma'}{(\gamma_b + \gamma')^2 + \omega_{2+}^2}. \quad (4.18)$$

In this situation  $W_{L1}$  becomes similar to the expression (3.26) and  $W = W_{BR} + W_{L1}$  is shown to be

$$W = 2W'_{a \rightarrow b1} \cdot \frac{\gamma'}{\gamma_b(\gamma_b + 2\gamma')} \cdot W'_{b2 \rightarrow c}. \quad (4.19)$$

This is a three-step transition  $A \rightarrow B_1 \rightarrow B_2 \rightarrow C$ . The first and the last factors correspond to the absorption process from  $A$  to  $B_1$  and emission from  $B_2$  to  $C$ , respectively. The middle factor represents the transition from  $B_1$  to  $B_2$ , because  $\gamma_{12}$  in eq. (4.14) becomes  $\gamma'$  in this limits. Thus, eq. (4.16) obviously corresponds to the luminescence process in this limit.

The total intensity of emission is calculated as

$$I = 2\pi |\langle b_2 | V_2 | c \rangle|^2 \cdot \mathfrak{W}_{ab1}^2 \left( \frac{\gamma_b + \gamma_m}{\gamma_b \cdot \gamma_m} - \frac{\gamma_{12}}{\gamma_b(\gamma_b + \gamma_{12})} \right). \quad (4.20)$$

#### 4.2 Model II

For this model, calculation is done in the same way as in the subsection 4.1. The final result is given by

$$W = W_R + W_{L2}, \quad (4.21)$$

where

$$W_R = |\langle a | V_1 | b_1 \rangle|^2 |\langle b_2 | V_2 | c \rangle|^2 2\pi \cdot \delta(\omega_1 - \omega_2) \cdot \frac{1}{(\gamma_b + \gamma(\omega_{1+}))^2 + (\omega_{1-} - \delta(\omega_{1+}))^2} \quad (4.22)$$

and

$$W_{L2} = 2 \mathfrak{W}_{ab1}^2 \left( \frac{\gamma_b + \gamma_m}{\gamma_b \cdot \gamma_m} - \frac{\gamma_{12}}{\gamma_b(\gamma_b + \gamma_{12})} \right) \mathfrak{W}_{b1c}^2. \quad (4.23)$$

Here,  $\mathfrak{W}_{ab1}^2$  is given by eq.(4.9) and  $\mathfrak{W}_{b1c}^2$  by

$$\mathfrak{W}_{b1c}^2 = W_{b1 \rightarrow c}^e \cdot \frac{\gamma(\omega_{2+})}{\gamma_b + \gamma(\omega_{2+})} \cdot \frac{\gamma_m}{\gamma_b + \gamma_m}, \quad (4.24)$$

$$W_{b1 \rightarrow c}^e = |\langle b_1 | V_2 | c \rangle|^2 \frac{\gamma_b + \gamma(\omega_{2+})}{(\gamma_b + \gamma(\omega_{2+}))^2 + (\omega_{2-} - \delta(\omega_{2+}))^2}. \quad (4.25)$$

The factors  $(\gamma_b + \gamma_m)/(\gamma_b \cdot \gamma_m)$  and  $\gamma_{12}/\gamma_b(\gamma_b + 2\gamma_{12})$  appearing in the middle part of eq. (4.23) coincide with middle part of eqs. (3.12) and (4.8), respectively. The presence of the second term is easy to understand because the transition from  $B_1$  to  $B_2$  by the perturbation  $\Omega$  is a loss for the luminescence.

In the static limit,  $W_{L2}$  vanishes and  $W$  is a Raman process

$$W = |\langle a | V_1 | b_1 \rangle|^2 |\langle b_2 | V_2 | c \rangle|^2 \times 2\pi \cdot \delta(\omega_1 - \omega_2) \frac{\gamma_b^2 + \omega_1^2 + \omega_0^2/4}{[\gamma_b^2 + (\omega_1 + \sqrt{\Delta^2 + \omega_0^2/4})^2][\gamma_b^2 + (\omega_1 - \sqrt{\Delta^2 + \omega_0^2/4})^2]}. \quad (4.26)$$

This equation is similar to eq. (4.15).

In the motional narrowing limit,  $W$  becomes

$$W = |\langle a | V_1 | b_1 \rangle|^2 |\langle b_2 | V_2 | c \rangle|^2 2\pi \cdot \delta(\omega_1 - \omega_2) \cdot \frac{1}{(\gamma_b + \gamma')^2 + \omega_{1-}^2} + W'_{a \rightarrow b1} \cdot \frac{\gamma'}{\gamma_b + \gamma'} \cdot \left[ \frac{1}{\gamma_b} - \frac{\gamma'}{\gamma_b(\gamma_b + 2\gamma')} \right] \cdot \frac{\gamma'}{\gamma_b + \gamma'} \cdot W'_{b1 \rightarrow c}, \quad (4.27)$$

where  $W'_{a \rightarrow b1}$  is given by eq. (4.17) and

$$W'_{b1 \rightarrow c} = |\langle b_1 | V_2 | c \rangle|^2 \cdot \frac{\gamma_b + \gamma'}{(\gamma_b + \gamma')^2 + \omega_{2-}^2}. \quad (4.28)$$

For the general value of  $\gamma_m$ , the total intensity of emission is written as

$$I = 2\pi |\langle b_1 | V_2 | c \rangle|^2 \cdot \left( \mathfrak{W}_{ab1}^2 \cdot \frac{\gamma_{12}}{\gamma_b(\gamma_b + \gamma_{12})} + W'_{a \rightarrow b1} \cdot \frac{1}{\gamma_b + \gamma(\omega_{1+})} \right). \quad (4.29)$$

#### 4.3 Model III

The result for this model is obtained by adding the result of models I and II. Then,  $W$  is writ-

ten by using eqs. (4.7), (4.8), (4.22) and (4.23) as

$$W = W_R + W_{BR} + W_{L1} + W_{L2}. \quad (4.30)$$

This intensity is composed of the factor corresponding to the transition from  $A$  to  $B$  and the damping factor in  $B$  levels as eq. (3.16).

In the static limit,  $W_{L1}$  and  $W_{L2}$  vanish and  $W = W_{BR} + W_R$  is given by

$$W = |\langle a | V_1 | b_1 \rangle|^2 \times 2\pi \cdot \delta(\omega_1 - \omega_2) \frac{|\langle b_2 | V_2 | c \rangle|^2 (\gamma_b^2 + \omega_1^2 + \omega_0^2/4) + |\langle b_1 | V_2 | c \rangle|^2 \Delta^2}{[\gamma_b^2 + (\omega_1 + \sqrt{\Delta^2 + \omega_0^2/4})^2][\gamma_b^2 + (\omega_1 - \sqrt{\Delta^2 + \omega_0^2/4})^2]}. \quad (4.31)$$

In the motional narrowing limit,  $W$  becomes

$$W = |\langle a | V_1 | b_1 \rangle|^2 |\langle b_2 | V_2 | c \rangle|^2 2\pi \cdot \delta(\omega_1 - \omega_2) \frac{1}{(\gamma_b + \gamma')^2 + \omega_{1-}^2} + 2W'_{a \rightarrow b1} \cdot \frac{\gamma'}{\gamma_b + \gamma'} \cdot \left( \left[ \frac{1}{\gamma_b} - \frac{\gamma'}{\gamma_b(\gamma_b + 2\gamma')} \right] \cdot \frac{\gamma'}{\gamma_b + \gamma'} \cdot W'_{b1 \rightarrow c} + \frac{\gamma'}{\gamma_b(\gamma_b + 2\gamma')} \cdot W'_{b2 \rightarrow c} \right). \quad (4.32)$$

Each term of this equation is composed of the factors corresponding to transitions  $A \rightarrow B_1$ ,  $B_1 \rightarrow B_2$ ,  $B_2 \rightarrow C$ , and branching factors as shown in Fig. 6.

For a finite value of  $\gamma_m$ , it seems that each term of eq. (4.30) can be interpreted in the same way as in the motional narrowing limit. However, as there is the quantum coherence in  $W_{BR}$ , the simple branching scheme is not applicable.

If we put  $\langle b_1 | V_2 | c \rangle = \langle b_2 | V_2 | c \rangle = \langle b | V_2 | c \rangle$ , eq. (4.31) becomes

$$W = W_R + W_{BR} = |\langle c | V_2 | b \rangle|^2 |\langle b_1 | V_1 | a \rangle|^2 2\pi \cdot \delta(\omega_1 - \omega_2) \frac{1}{2} \left( \frac{1}{\gamma_b^2 + (\omega_1 + \sqrt{\Delta^2 + \omega_0^2/4})^2} + \frac{1}{\gamma_b^2 + (\omega_1 - \sqrt{\Delta^2 + \omega_0^2/4})^2} \right). \quad (4.33)$$

This equation contains two terms factors corresponding to two eigenstates. In this case, the total intensity of emission which is given by adding eqs. (4.20) and (4.29) becomes

$$I = 2\pi |\langle c | V_2 | b \rangle|^2 W_{a \rightarrow b1} \frac{1}{\gamma_b}. \quad (4.34)$$

If we put  $\omega_0 = 0$ , the solution eq. (4.30) agree with eq. (3.9). This is easily understood

as follows: The eigenstates of  $H$  (eq. (4.3)) are given by  $|b_{\pm}\rangle = (|b_1\rangle \pm |b_2\rangle)/2$  with eigenvalues  $b \pm \Delta$ . Though  $V_1$  connects  $a$  with both  $|b_+\rangle$  and  $|b_-\rangle$ ,  $V_2$  connects  $|c\rangle$  with only  $|b_+\rangle$ . Thus, the present model reduces to the model discussed in §3 and eq. (4.30) reduce to eq. (3.9).

Figures 7-9 illustrate the spectral distributions of  $W_{BR}$ ,  $W_{L1}$  and  $W_{L2}$  normalized by the

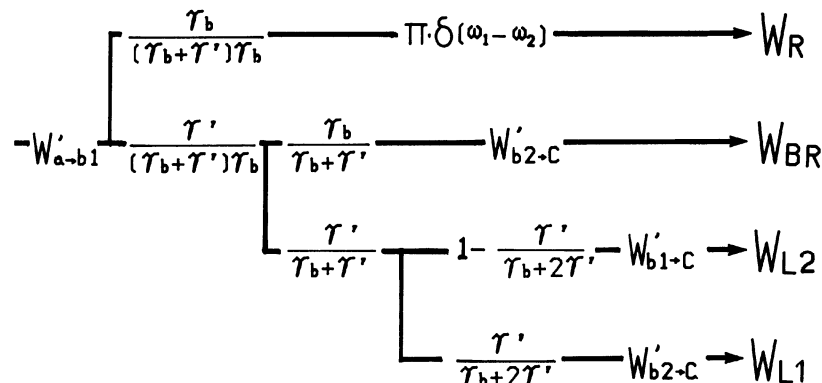


Fig. 6. Branching features of the spectrum of four-level atom in the motional narrowing limit. The factors  $W'_{a \rightarrow b1}$ ,  $W'_{b1 \rightarrow c}$  and  $W'_{b2 \rightarrow c}$  are defined by eqs. (4.17), (4.18) and (4.28).

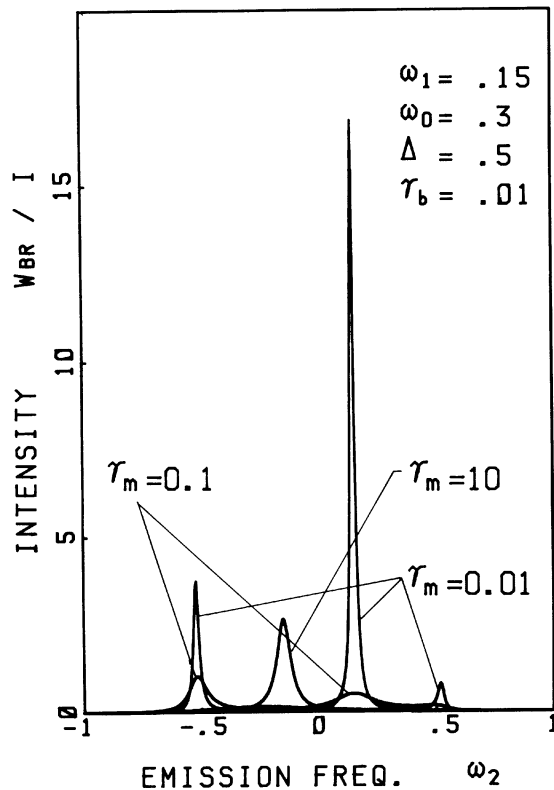


Fig. 7. Emission spectra of the broadened Raman term of four-level atom with an off-diagonal modulation.

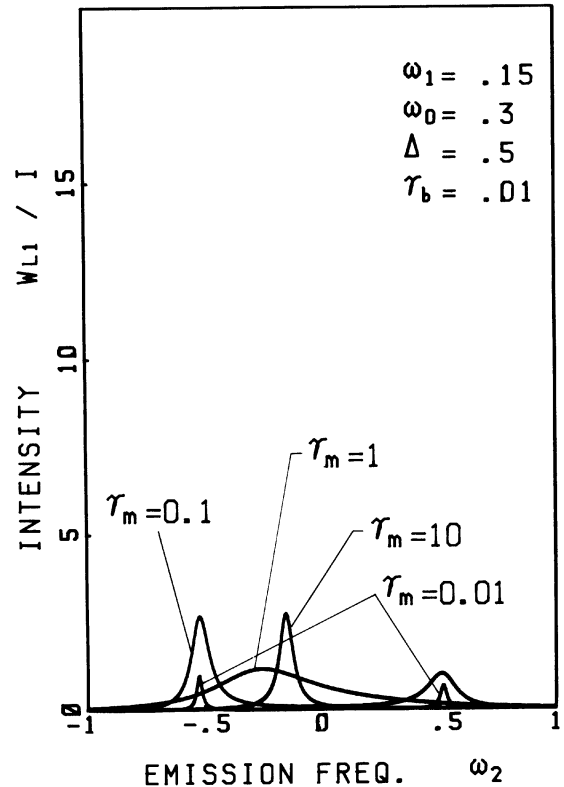


Fig. 8. Emission spectra of the luminescence term  $W_{L1}$  of four-level atom with an off-diagonal modulation.

total intensity, respectively. We set  $\omega_1=0.15$ ,  $\Delta=0.15$ ,  $\Delta=0.5$  and  $\gamma_b=0.01$  as in Figs. 3 and 4. The excited states are separated by  $\omega_0=0.3$ . For small values of  $\gamma_m$ ,  $W_{L1}$  and  $W_{L2}$  show two peaks at frequencies of two eigen states of eq. (4.3), respectively. In Fig. 8, the left peak of  $W_{L1}$ , which corresponds to the frequency of eigen state near  $B_2$ , is higher than the right, because  $B_2$  and  $C$  are connected directly by  $V_2$  in the model I. Similarly, the right peak of  $W_{L2}$  is higher than the left in Fig. 9. When  $\gamma_m$  becomes larger, two peaks of  $W_{L1}$  merge into a single peak at the frequency of  $\omega_2 = -\omega_0/2$  and those of  $W_{L2}$  at  $\omega_2 = \omega_0/2$ , as they are motionally narrowed.

§5. Conclusion

We have treated the second order optical processes in three- and four-level atoms in which the excited states are perturbed by two-state random modulations. This simplification of the models made it possible to obtain the results in algebraic expressions. The spectrum of emitted light is in each case shown to be divided into three terms, namely the pure Raman term  $W_R$ , the broadened Raman term

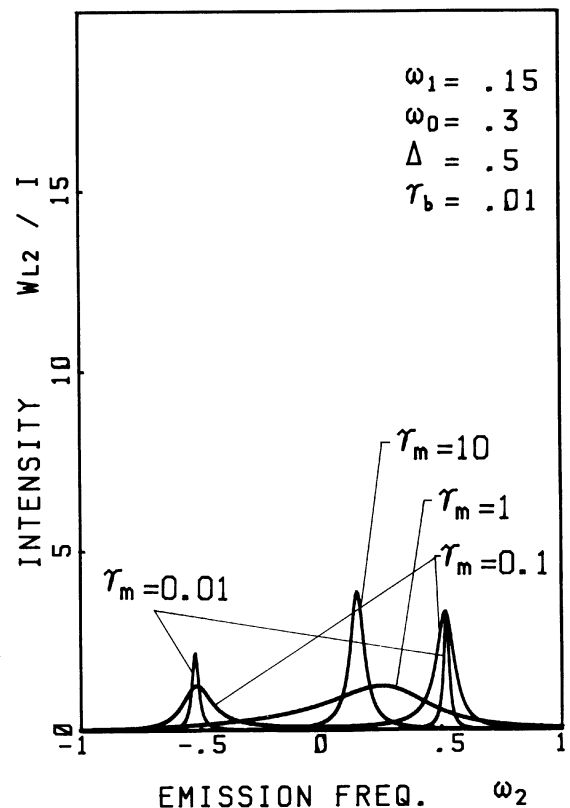


Fig. 9. Emission spectra of the luminescence term  $W_{L2}$  of four-level atom with off-diagonal modulation.

$W_{BR}$  and the pure luminescence term  $W_L$ . The pure Raman term yields a sharp Raman spectrum of the delta-function type which cor-

responds to a coherent process from the initial to the final state through the intermediate excited states. The pure luminescence term gives the spectrum of spontaneous emission by transitions from the excited states to the final state which is incoherent with the absorption process from the initial to the excited states. The main factors appearing in this term are proportional to the rates of quantum transitions of absorption and emission but differ from them by the factors shown in eqs. (3.13) and (3.14). This difference seems to be due to the presence of the term which we called the broadened Raman term. This term contributes to the pure Raman scattering in the limit of static modulation and to the pure luminescence in the other limit of motional narrowing where the modulation rate is faster than any of other rate parameters. In the latter limit the resultant of  $W_{BR}$  and  $W_L$  gives the luminescence expressed by a product of the rates of absorption, emission and transition among the ex-

cited states. This is naturally to be expected. In the medium values of the modulation rate, the term  $W_{BR}$  bears a mixed character of Raman and luminescence, which cannot be distinctly separated. Generally, the incoherent part is more pronounced when the incident light is closer to the resonance. When it is far off-resonance, the coherent Raman part dominates.

We conjecture that these features elucidated here for the particular model of two-state jump modulation are common for more general cases of stochastic models although it is difficult to achieve explicit separation of the emission spectra. Also we limited ourselves here to CW cases. Extension of the analysis to the cases of pulsed excitation is important and is interesting. We leave it for a future study.

### Appendix

The terms in eq. (3.7) can be calculated by using the following formula;

$$\begin{aligned} \left(0 \left| \frac{1}{\gamma_b + \Gamma + i(\omega - \Omega)} \right| 0\right) &= \left(0 \left| \frac{1}{\gamma_b + \Gamma + i\omega} \right| 0\right) + \left(0 \left| \frac{1}{\gamma_b + \Gamma + i\omega} \right| 0\right) \\ &\quad \times (0 | i\Omega | 1) \left(1 \left| \frac{1}{\gamma_b + \Gamma + i\omega} \right| 1\right) (1 | i\Omega | 0) \left(0 \left| \frac{1}{\gamma_b + \Gamma + i\omega} \right| 0\right) \\ &\quad + \dots \\ &= \left(0 \left| \frac{1}{\gamma_b + \Gamma + i\omega - (0 | i\Omega | 1) \left(1 \left| \frac{1}{\gamma_b + \Gamma + i\omega} \right| 1\right) (1 | i\Omega | 0)} \right| 0\right) \\ &= \frac{1}{\gamma_b + \gamma(\omega) + i(\omega - \delta(\omega))}, \end{aligned} \quad (\text{A} \cdot 1)$$

and

$$\begin{aligned} \left(0 \left| \frac{1}{\gamma_b + \Gamma + i(\omega - \Omega)} \right| 1\right) &= \left(0 \left| \frac{1}{\gamma_b + \Gamma + i\omega} \right| 0\right) (0 | i\Omega | 1) \left(1 \left| \frac{1}{\gamma_b + \Gamma + i\omega} \right| 1\right) \\ &= \frac{1}{\gamma_b + \gamma(\omega) + i(\omega - \delta(\omega))} \frac{i\Delta}{\gamma_b + \gamma_m + i\omega}, \end{aligned} \quad (\text{A} \cdot 2)$$

with

$$\gamma(\omega) = \frac{(\gamma_b + \gamma_m)\Delta^2}{(\gamma_b + \gamma_m)^2 + \omega^2} \quad \text{and} \quad \delta(\omega) = \frac{\omega\Delta^2}{(\gamma_b + \gamma_m)^2 + \omega^2}. \quad (\text{A} \cdot 3)$$

### References

- 1) L. Huber: Phys. Rev. **158** (1967) 843.
- 2) L. Huber: Phys. Rev. **170** (1968) 418.
- 3) L. Huber: Phys. Rev. **178** (1969) 93.
- 4) L. Huber: Phys. Rev. **B1** (1970) 3409.
- 5) A. Nitzan and J. Jortner: J. Chem. Phys. **57** (1972) 2870.

- 6) S. Mukamel, A. Ben-Reuven and J. Jortner: *Phys. Rev. A* **12** (1975) 947.
  - 7) S. Mukamel and A. Nitzan: *J. Chem. Phys.* **66** (1977) 2462.
  - 8) S. Mukamel: *J. Chem. Phys.* **71** (1979) 2884.
  - 9) Y. Toyozawa: *J. Phys. Soc. Jpn.* **41** (1976) 400.
  - 10) A. Kotani and Y. Toyozawa: *J. Phys. Soc. Jpn.* **41** (1976) 1699.
  - 11) R. Kubo, T. Takagawara and E. Hanamura: *Proc. Oji Seminar Physics of Highly Excited States* (Springer Verlag, Heidelberg, 1976) p. 304.
  - 12) T. Takagawara, E. Hanamura and R. Kubo: *J. Phys. Soc. Jpn.* **43** (1977) 802.
  - 13) T. Takagawara, E. Hanamura and R. Kubo: *J. Phys. Soc. Jpn.* **43** (1977) 811.
  - 14) T. Takagawara, E. Hanamura and R. Kubo: *J. Phys. Soc. Jpn.* **43** (1977) 1522.
  - 15) T. Takagawara, E. Hanamura and R. Kubo: *J. Phys. Soc. Jpn.* **44** (1978) 728.
  - 16) T. Takagawara, E. Hanamura and R. Kubo: *J. Phys. Soc. Jpn.* **44** (1978) 742.
  - 17) T. Takagawara: Dr. Thesis, Dep. Physics, Univ. of Tokyo, 1976.
  - 18) R. Kubo: *Pure & Appl. Chem.* **57** (1985) 201.
  - 19) R. Kubo: *Stochastic Progress in Chemical Physics* (John Wiley & Sons, 1969) p. 101.
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