STOCHASTIC MODELS OF INTERMEDIATE STATE INTERACTION IN SECOND ORDER OPTICAL PROCESSES

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ABSTRACT

The stochastic theory of spectral line shape as developed by one of the present authors is here extended to the problem of intermediate state interaction in a second order optical process. Depending on the stochastic nature of the interaction, the process may appear as a pure Raman process, or a luminescent process, or a mixed process. Simple but standard models are 1) the adiabatic random modulation and 2) the off-diagonal random modulation of the intermediate states. Limiting cases of slow and fast modulation are discussed in a general way. Some model calculations are made in order to see how a spectrum changes its nature from one limit to another.

I. INTRODUCTION

In the course of an optical process, the system under observation may interact with its environment. An interaction present in the initial or the final state of the process is called an initial or a final state interaction, and affects the line shape of the absorption or the emission spectrum of the system. The nature of such an effect is pretty well understood by now. On the other hand, the role of an intermediate state interaction, which will be abbreviated as IMSI in the following, seems to be a matter of controversy, as is seen in a number of recent papers on the relationship between a resonant Raman process and a luminescent process.[1)]

In order to look into the essential points of this sort of problem,

it is generally advantageous to simplify the problem somewhat by regarding the interaction as a random modulation acting on the system in question. This is the spirit of stochastic theories of line shape, as developed some years ago by one of the present authors and by many other authors.[2-5] Such theories have been, however, so far limited mostly to the initial or the final state interactions in the first order processes.

The aim of the present work is to extend a stochastic theory to the intermediate state interactions and to study how a second order optical spectrum is affected by an IMSI. It will be shown that the spectrum bears simple characters in some ideal limits of the stochastic IMSI. If the model is simple enough, it is also possible to study in more detail how the spectrum changes its character as the random IMSI changes from the limit of slow modulation to the other limit of fast modulation. Such a treatment of stochastic models of IMSI is useful for obtaining a deeper insight into the second order optical processes. Since the work is still in progress, this is rather a sketchy report of the results so far obtained. A more complete paper will be published elsewhere in the near future.

II. GENERAL FORMULATION

We consider a system, denoted by S, in contact with its environment R and the photon field Φ. The quantum states and their energies of S are denoted by A, B, and C, and the photon numbers by n_1, n_2, ... The Hamiltonian of the total system is written as

$$\mathcal{H} = H + H_{\Phi} + V \quad , \tag{1}$$

where

$$H = H_S + H_R + H_{SR} \tag{2}$$

is the Hamiltonian for the system S + R, H_{SR} being the interaction between S and R, H_Φ the Hamiltonian of Φ, and V is the interaction of S with the photon field,

$$V = V_1^+ + V_1^- + V_2^+ + V_2^- + \cdots \quad . \tag{3}$$

The interaction $V_1^\pm$ creates or annihilates a photon ω_1 and combines the state A with B. Likewise $V_2^\pm$ creates or annihilates a photon ω_2 and combines C with B. Thus in a second order process starting from the initial state,

$$|a\rangle = |A, n_1+1, n_2, \ldots\rangle \quad \text{with the energy} \quad a = A + \omega_1 ,$$

and ending at the final state,

$$|c\rangle = |C, n_1, n_2+1, \ldots\rangle \quad \text{with the energy} \quad c = C + \omega_2 ,$$

a photon ω_1 is absorbed and a photon ω_2 is emitted. The energy of the photon field is referred to the state $(n_1, n_2, \ldots)$. In the intermediate states, S is in B and photon numbers are either $(n_1, n_2, \ldots)$ or $(n_1+1, n_2+1, \ldots)$. We ignore the latter state because we shall be mainly interested in the near resonance situation,

$$A + \omega_1 \sim B, \quad \text{or} \quad C + \omega_2 \sim B, \tag{4}$$

which may cause a real absorption process from A to B or a real emission process from B to C.

Since we focus our attention on the IMSI, the interaction H_{SR} is assumed to be present only in the state(s) B. The environment R is in an equilibrium at the initial time and is described by a density matrix ρ_R^e. It evolves in its own way throughout the whole process and causes a random modulation on S through the interaction H_{SR}.

The equation of motion of the density matrix of the total system,

$$i \frac{\partial \rho}{\partial t} = [\mathcal{H}, \rho], \tag{5}$$

is solved by iteration with the initial condition,

$$\rho(0) = |a\rangle \langle a| \times \rho_R^e \quad . \tag{6}$$

The solution gives the probability $P(t)$ of finding the final state c at time t as

$$P(t) = \int_0^t dt_1 \int_0^{t_1} dt_2 \int_0^t dt_1' \int_0^{t_1'} dt_2'$$

$$\times Tr_R \langle c | e^{-i(H+\omega_2)(t-t_1)} V_2^+ e^{-iH(t_1-t_2)} V_1^- e^{-i(H+\omega_1)t_2} | a\rangle \rho_R^e$$

$$\times \langle a | e^{i(H+\omega_1)t_2'} V_1^+ e^{iH(t_1'-t_2')} V_2^- e^{i(H+\omega_2)(t-t_1')} | c\rangle \quad . \tag{7}$$

In this expression, propagation of the states is governed by the Hamiltonian (2). More rigorously, we could have included an appropriate part of the total Hamiltonian in the propagators, which should give rise to the radiative damping or other sorts of damping effective in bringing the system out of the states under consideration. Instead of doing such an explicit treatment of damping, we take here a somewhat phenomenological approach in this respect by introducing an effective damping γ_b for the intermediate state b. Namely the propagators in the intermediate states $\exp[-iH(t_1 - t_2)]$ and $\exp[iH(t_1' - t_2')]$ are replaced by

$$e^{-(iH+\gamma_b)(t_1-t_2)} \quad \text{and} \quad e^{(iH-\gamma_b)(t_1'-t_2')} \quad ,$$

to take account of such damping. It should be emphasized that this damping is assumed to be caused by some mechanism other than the intermediate state interaction on which we focus our attention.

If the probability $P(t)$ is evaluated for a proper range of t, it will be of the form,

$$P(t) = W_1 t + W_2 t^2 + \ldots \quad . \tag{8}$$

Then the transition rate of the two-photon process is identified with W_1, which coincides in usual cases with the answer given by the golden rule. A question arises here whether or not a two-step process like a luminescence is ever contained in this calculation of the transition rate. In fact, a simple consideration shows that it is the case if the above-mentioned damping rate γ_b is large in comparison with the rate of real absorption or emission. If we write simple rate equations as

$$\dot{P}_a = - \lambda_{ab} P_a \ ,$$

$$\dot{P}_b = \lambda_{ab} P_a - \lambda_{bc} P_b - 2 \gamma_b P_b \ ,$$

$$\dot{P}_c = \lambda_{bc} P_b \ ,$$

and evaluate $P_c(t)$ for the initial condition,

$$P_a(0) = 1, \ P_b(0) = P_c(0) = 0 \ ,$$

we find that

$$P_c(t) \sim \frac{\lambda_{ab} \ \lambda_{bc}}{2 \ \gamma_b} t \qquad \text{for} \quad \gamma_b^{-1} \ll t \ll \lambda_{ab}^{-1}, \lambda_{bc}^{-1} \ , \tag{9}$$

if γ_b is much larger than other time rates. On the other hand, if $\gamma_b = 0$, we have only

$$P_c(t) \sim \frac{1}{2} \lambda_{ab} \ \lambda_{bc} \ t^2 \quad \text{for} \quad t \ll \lambda_{ab}^{-1}, \lambda_{bc}^{-1} \ . \tag{10}$$

We now observe the following. The integrand of the expression (7), which we call the propagator of the second order process, is a function of the four time points ($t_2 < t_1$, $t_2' < t_1'$), independent of t, and furthermore is invariant with respect to translations along the time axis. This means that the Laplace transform of P(t) has the form,

$$F(s) = \int_0^\infty dt\ e^{-st}\ P(t) = \frac{F_1(s)}{s^2} + \ldots \quad ,$$

and the transition rate is obtained by

$$W_1 = \lim_{s\to+0} F_1(s)$$

$$= \lim_{s\to+0} \int_0^\infty d\tau\ e^{-s\tau} \int_0^\tau d\tau_1 \int_0^{\tau_1} d\tau_2\ (\mathrm{I} + \mathrm{II} + \mathrm{III} + \mathrm{c.c.}). \qquad (11)$$

Here I, II, and III are decompositions of the original propagator of the second order process and are schematically represented by the graphs shown in Fig. 1. The four time points appear in eq.(7) in different types of order. The earliest of them can be chosen as the origin of time and the latest is called τ, so that now the four time points are renamed as $(0, \tau_2, \tau_1, \tau)$ according to their order on the time axis. The upper arcs in each graph refer to propagation to the right and lower arcs to the left, in eq.(7), starting from the initial state and ending at the final state. Each of arcs is associated with a particular state of the system. The structure of these decomposed propagators will be seen in the examples to be discussed in the following.

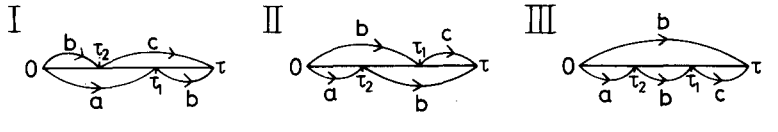

Fig.1. Decomposed propagators of a second order process.

III. A THREE LEVEL SYSTEM WITHOUT IMSI

As a standard example, we now consider a three level system without IMSI. From the graphs in Fig. 1, explicit forms of the propagators can be written down immediately by noticing that the phase factors for each of the time intervals $(0, \tau_2)$, (τ_2, τ_1) and (τ_1, τ) are determined

by the difference of energies of propagation on the upper and lower arcs. Thus we have

$$I_0 = \exp[-(\gamma_b+i(b-c))(\tau-\tau_1)-i(a-c)(\tau_1-\tau_2)-(\gamma_b+i(a-b))\tau_2] \quad ,$$

$$II_0 = \exp[-(\gamma_b+i(b-c))(\tau-\tau_1)-2\gamma_b(\tau_1-\tau_2)-(\gamma_b+i(a-b))\tau_2] \quad ,$$

$$III_0 = \exp[-(\gamma_b+i(c-b))(\tau-\tau_1)-2\gamma_b(\tau_1-\tau_2)-(\gamma_b+i(a-b))\tau_2] \quad , \qquad (12)$$

omitting the coefficient $|V_1|^2|V_2|^2$ hereafter. Equation (11) gives

$$W_1 = \lim_{s\to+0}\Big[\frac{1}{\gamma_b+i(b-c)}\,\frac{1}{s+i(a-c)}\,\frac{1}{\gamma_b+i(a-b)} \qquad \text{(I)}$$

$$+ \frac{1}{\gamma_b+i(b-c)}\,\frac{1}{2\gamma_b}\,\frac{1}{\gamma_b+i(a-b)} \qquad \text{(II)}$$

$$+ \frac{1}{\gamma_b+i(c-b)}\,\frac{1}{2\gamma_b}\,\frac{1}{\gamma_b+i(a-b)} \qquad \text{(III)}$$

$$+ \text{c.c.}\Big] \quad . \qquad (13)$$

The evaluation assumes $s \ll \gamma_b$ or $t \gg \gamma_b^{-1}$. By the relation,

$$\frac{1}{s+i(a-c)} = \pi\delta(a-c) - \frac{i}{a-c} \quad ,$$

the first term and its c.c. in eq.(13) yield a Raman term containing a delta-function and a negative term. As is expected from the conservation of energy, the latter term is exactly cancelled out by the contribution from the other terms, which amounts to

$$\gamma_b/\{\gamma_b^2 + (b-a)^2\}\{\gamma_b^2 + (c-b)^2\} \quad . \qquad (14)$$

So we are left with the pure Raman term,

$$W_1 = \pi\delta(a-c)\,\frac{\gamma_b^2 + (b-a)(b-c)}{\{\gamma_b^2+(b-a)^2\}\{\gamma_b^2+(b-c)^2\}} \qquad (15)$$

$$= \frac{\pi\delta(A-C+\omega_1-\omega_2)}{\gamma_b^2 + (B-A-\omega_1)^2} \quad .$$

IV. ADIABATIC RANDOM MODULATION IN IMSI

The environment R is now supposed to exert a random perturbation on S in its intermediate state. The simplest model of this is a random adiabatic shift of B. Thus we assume

$$b(t) = \bar{b} + b'(t), \quad \overline{b'(t)} = 0 \quad , \tag{16}$$

where $b(t)$ is a random process, $\bar{b}$ being the time-averaged intermediate level, and $b'(t)$ the fluctuation. This causes random phase modulation of propagators. From the graphs in Fig. 1, it is seen that the modulation works in the intervals $(0, \tau_2)$ and (τ_1, τ) but not in (τ_2, τ_1). It should be kept in mind, however, that the random modulation persists throughout the whole time interval $(0, \tau)$ even if it is inactive in the middle.

Now the propagators are modified by a common modulation factor,

$$F(\tau_2,\tau_1,\tau) = \langle \exp\left[i \int_0^{\tau_2} b'(t)dt - i \int_{\tau_1}^{\tau} b'(t)dt \right] \rangle \quad , \tag{17}$$

where the average is taken over all possible realizations of $b'(t)$. Without making any explicit calculations, we can see immediately what happens in the following two limits.

a) SLOW MODULATION LIMIT. If the modulation is very slow, the adiabatic modulation is static. The problem is essentially the same as that discussed in section III except that the intermediate level has a probability distribution, say $P(b)$. Thus the transition rate W_1 should be

$$W_1 = \pi\delta(a-c) \int db\ P(b) \frac{\gamma_b^2+(b-a)(b-c)}{\{\gamma_b^2+(b-a)^2\}\{\gamma_b^2+(c-b)^2\}} \quad ,$$

which is a pure Raman process.

b) FAST MODULATION LIMIT (NARROWING LIMIT). If the modulation is fast enough to satisfy the narrowing condition, the random phase modulation reduces to a phase memory relaxation familiar in spin resonance phenomena. In our case, the phase modulation factor given by eq.(17) becomes

$$F(\tau_2,\tau_1,\tau) = \exp\{-\gamma'\tau_2 - \gamma'(\tau-\tau_1)\} \quad , \tag{18}$$

where

$$\gamma' \sim \langle (b')^2 \rangle \tau_m \qquad \left(\tau_m = \gamma_m^{-1}\right)$$

is the effective transverse relaxation rate of the phase memory. This approximation is valid if the correlation time τ_m of the random IMSI is so short as to satisfy the narrowing condition,

$$\langle (b')^2 \rangle^{\frac{1}{2}} \tau_m \ll 1 \quad ,$$

and if the resulting spectrum of W_1 is broad enough. In this narrowing limit the afore-mentioned cancellation of non-Raman term is no longer complete and we are left with

$$W_1 = \pi\delta(a-c)\,\frac{\gamma^2+(\bar{b}-a)(\bar{b}-c)}{\{\gamma^2+(\bar{b}-a)^2\}\{\gamma^2+(\bar{b}-c)^2\}} + \frac{\gamma'}{\gamma_b(\gamma_b+\gamma')}\,\frac{\gamma}{\{\gamma^2+(\bar{b}-a)^2\}}\,\frac{\gamma}{\{\gamma^2+(\bar{b}-c)^2\}} \quad , \tag{19}$$

where

$$\gamma = \gamma_b+\gamma' \quad .$$

Here we have, besides the Raman term, a luminescence-like continuous spectrum inversely proportional to γ_b, in accordance with eq.(9). Its spectral function is the product of the resonance absorption factor and the resonant emission factor, which seems quite natural. For a vanish-

ing τ_m, everything is averaged out and only the Raman term remains.

In general cases of arbitrary rate of random modulation, it is necessary to define the problem more explicitly. As was discussed in a review article some years ago by one of the present authors,[2] it is possible to develop a general treatment if the random modulation is assumed to be basically Markoffian. Two standard examples are considered here.

1) TWO-STATE JUMP MODEL. The modulation $b'(t)$ in eq.(16) is assumed to take only two values, $b' = \pm\Delta$ corresponding to two possible states of R. This is of course a great idealization, but is sufficient to reveal some general features of the problem. The two states,

$$|+) = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \text{and} \quad |-) = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \quad ,$$

alternate randomly as a Markoffian process characterized by the transition matrix,

$$\Gamma = \frac{\gamma_m}{2} \begin{pmatrix} -1 & 1 \\ 1 & -1 \end{pmatrix} \quad , \tag{20}$$

and the random modulation is represented by the matrix,

$$\Omega = \begin{pmatrix} \Delta & 0 \\ 0 & -\Delta \end{pmatrix} \quad . \tag{21}$$

Following the general formalism of such Markoffian random modulation, we easily find that the transition rate W_1 is given by the formula,

$$\begin{aligned} W_1 = \lim_{s\to+0} \Big[& (0| \frac{1}{\gamma_b+i(\bar{b}-c)+i\Omega-\Gamma} \frac{1}{s+i(a-c)-\Gamma} \frac{1}{\gamma_b+i(a-\bar{b})-i\Omega-\Gamma} |0) \\ & +(0| \frac{1}{\gamma_b+i(\bar{b}-c)+i\Omega-\Gamma} \frac{1}{2\gamma_b-\Gamma} \frac{1}{\gamma_b+i(a-\bar{b})-i\Omega-\Gamma} |0) \\ & +(0| \frac{1}{\gamma_b+i(c-\bar{b})-i\Omega-\Gamma} \frac{1}{2\gamma_b-\Gamma} \frac{1}{\gamma_b+i(a-\bar{b})-i\Omega-\Gamma} |0) \end{aligned}$$

$$+ \text{c.c.} \;] \quad , \tag{22}$$

which is a generalization of eq.(13). Here each factor inside brackets is a two by two matrix and the initial state of R is the vector,

$$|0) = \frac{1}{2} \begin{pmatrix} 1 \\ 1 \end{pmatrix} \quad ,$$

corresponding to the equilibrium eigenvector of Γ. Multiplication by $(0| = (1, 1)$ from the left is summation over the final states of R. The right and left vectors $|0)$ and $(0|$ satisfy

$$\Gamma |0) = 0 \quad , \quad (0|\Gamma = 0 \; .$$

Evaluation of W_1 by eq.(22) is an elementary algebraic manipulation.

2) GAUSSIAN-MARKOFFIAN MODULATION. The modulation $b'(t)$ is assumed to be a Gaussian-Markoffian process, which is characterized by the correlation function,

$$\langle b'(t_1)b'(t_2)\rangle = \Delta^2 \exp\left[-\gamma_m | t_1 - t_2 | \right] \; . \tag{23}$$

The explicit form of the modulation factor eq.(17) is easily found to be

$$F_{\pm}(\tau_2, \tau_1, \tau) = \exp\left[- \frac{\Delta^2}{\gamma_m^2} \{ \gamma_m \tau_2 - 1 + e^{-\gamma_m \tau_2} + \gamma_m(\tau - \tau_1) - 1 \right.$$
$$\left. + e^{-\gamma_m(\tau - \tau_1)} \pm e^{-\gamma_m(\tau_1 - \tau_2)} (1 - e^{-\gamma_m \tau_2})(1 - e^{-\gamma_m(\tau - \tau_1)}) \} \right] . \tag{24}$$

With the definitions of eqs.(12) and (24), the propagators I, II and III are expressed as I_0F_-, II_0F_- and III_0F_+, respectively. Equation (11) enables us to calculate W_1. It should be noted that the expression (22) is generally valid for a Markoffian modulation, not only for a two-state jump model. For a Gaussian-Markoffian modulation, Ω in this expression is considered as a real continuous variable and Γ is the diffusion operator,

$$\Gamma = \gamma_m \left[\frac{\partial}{\partial \Omega} \Omega + \Delta^2 \frac{\partial^2}{\partial \Omega^2} \right] \quad . \tag{25}$$

The vectors $|0)$ and $(0|$ are eigenfunctions of Γ corresponding to the zero eigenvalue. Although the expression is compact, further analytical treatment is rather complicated, so that we have to work numerically.

Figures 2 and 3 are the results of such model calculations to show how the emission spectra vary as the rate of modulation changes from the slow limit to the fast limit. In each case, the levels A and C are taken at the same energy. The energies are normalized by the energy difference between these levels and the average energy $\bar{b}$ of the intermediate state B.

Figure 2 is for a two-state jump model. The state B randomly takes either of the two energies 0.8 and 1.2. The incident photon ω_1 is 1.5. The pure Raman peak with the delta-function $\delta(\omega_2 - 1.5)$ is omitted in the figure. When the modulation is slow with $\gamma_m = 0.01$, three resonance peaks are seen; one is a somewhat broadened Raman resonance which superposes on the delta-function peak and the other two peaks are in resonance with two possible excited levels and bear the character of luminescence. As the modulation becomes faster, say $\gamma_m = 0.1$ or 1.0, the narrowing takes place, which reduces the broad Raman-like peak and narrows the luminescence-like peaks into a sharp single peak at $\omega_2 = 1.0$ which finally disappears for $\gamma_m = \infty$.

Figure 3 is for a Gaussian model. The energy of the incident photon ω_1 is taken as 0.7. The general features are almost the same as the previous one. For slow modulation, a broadened Raman-like peak and a luminescence peak are seen. As the modulation becomes faster, the Raman-like peak disappears and the luminescence peak narrows. Both in Figs. 2 and 3, the zero-width Raman line, which is not shown in the figure, persists all the way. As is given in the figure caption, the intensity of this part does not so much vary with the rate of modulation through the slow and fast modulation limits.

Although the above results are obtained for some idealized models, the qualitative features should be common for more general cases of adiabatic modulation.

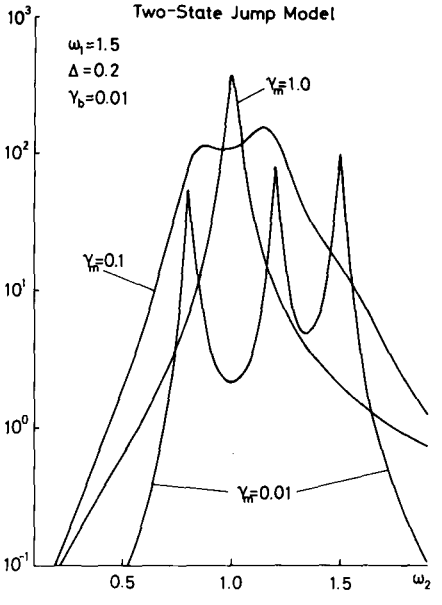

Fig.2. Emission spectra of a three-level system with adiabatic random modulation in a two-state jump model. The incident photon energy, the radiative damping rate and the rate and amplitude of modulation is denoted by ω_1, γ_b, γ_m and Δ, respectively. The emission intensity is plotted in an arbitrary scale. The intensity of the delta-function like Raman peak at ω_2=1.5, which is omitted in the figure, is given as 3.997×10^{1}, 3.758×10^{1} and 2.871×10^{1} for γ_m=0.01, 0.1 and 1.0, respectively.

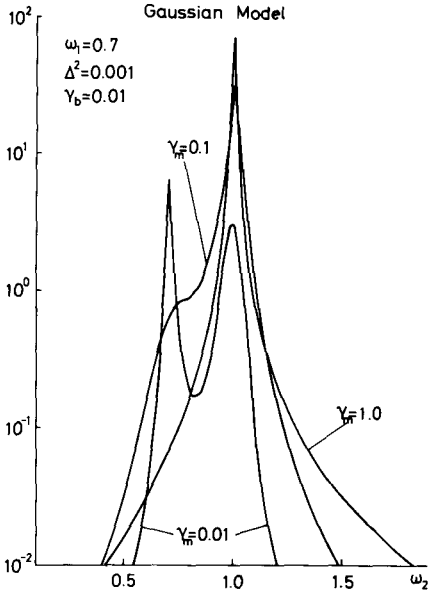

Fig.3. Emission spectra of a three-level system with adiabatic random modulation in a Gaussian-Markoffian model. Notations are the same as in Fig.2. The intensity of the zero-width Raman line at ω_2 =0.7, which is not shown in the figure, is given as 3.567×10^{1}, 3.555×10^{1} and 3.492×10^{1} for γ_m=0.01, 0.1 and 1.0, respectively.

V. OFF-DIAGONAL RANDOM MODULATION

The stochastic theory can be extended to more complex and more realistic models. The task is left for future studies. Here we

mention a simple model which may still simulate certain cases of physical interest. Suppose that the state B consists of two levels and the modulation from R acts as an off-diagonal random perturbation. Namely, the Hamiltonian for B is assumed to be

$$H_B = \begin{pmatrix} b_1 & \Omega(t) \\ \Omega(t) & b_2 \end{pmatrix} \quad , \tag{26}$$

where $\Omega(t)$ is a random process. Furthermore we assume that $V_1^{\pm}$ connects A with B_1 and $V_2^{\pm}$, C with B_2. Thus, in the absence of modulation, there is no way of a second order process between A and C. When $\Omega(t)$ is very slow, the states B_1 and B_2 are mixed and A and C are connected, giving rise to a Raman resonance in proportion to Ω^2. In the limit of extremely fast modulation, $\Omega(t)$ is averaged out and there is no second order process. For intermediate rates of modulation, there occur the adiabatic and the nonadiabatic effects of modulation. If the condition,

$$\gamma_m \ll E = |b_1 - b_2| \quad ,$$

is met, the effect is adiabatic and is similar to that discussed in the previous section. The only difference is that the Raman process is caused here by the off-diagonal modulation so that the resonance is broadened; there is no zero-width line. If γ_m approaches E, the power spectrum of modulation contains components which resonate with E to induce nonadiabatic transitions between B_1 and B_2. This causes a three-step transition, $A \rightarrow B_1$, $B_1 \rightarrow B_2$, $B_2 \rightarrow C$, a typical luminescence process, emitting $\omega_2 \sim B_2 - C$ when photons $\omega_1 \sim B_1 - A$ are absorbed in resonance. This model can be analysed in more detail if the process $\Omega(t)$ is specified, for example, as a two-state jump model. Figure 4 shows a model calculation of this type. For the slow modulation, excited states are shifted adiabatically to the levels at 1.672 and 0.628 for the set of parameters given in the figure. Since C = 0.1,

the Raman resonance peaks around $\omega_2 = 1.2$, and luminescent resonances are at 1.572 and 0.528. As the modulation becomes faster, the Raman peak decreases while the luminescent peaks dominate and coalesce into a single peak. These features are naturally understandable.

VI. CONCLUSION

Summarizing, we have shown that the effect of IMSI on a second order process can be studied by modeling it as a stochastic modulation. It is seen that the Raman-like and luminescence-like resonances may coexist in the emission spectra and the spectral shapes vary as the rate of modulation changes. This approach seems useful for understanding the nature of second order processes and the role of IMSI. Of course it is desired to clarify its relations to other theories. This is left for a future study.

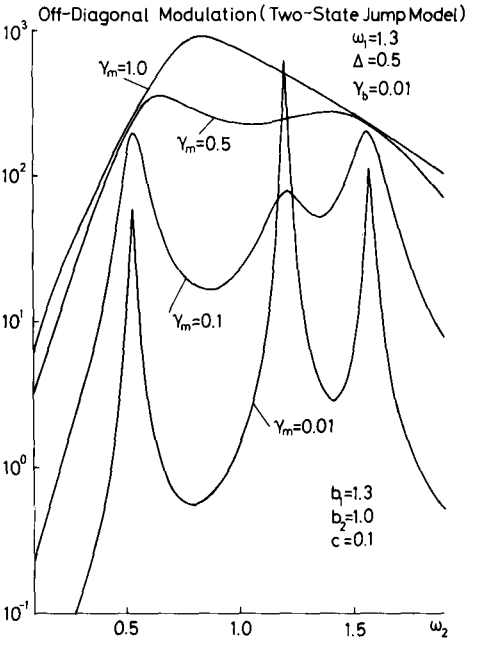

Fig.4. Emission spectra of a four-level system with off-diagonal modulation in a two-state jump model. The energy of the levels B_1, B_2 and C is denoted by b_1, b_2 and c, respectively. The level B_1 is optically connected only with the ground state A and the level B_2, only with C. The incident photon energy ω_1 is just resonant with the level B_1. There is no delta-function like Raman peak.

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