

## EXCITONIC MOLECULE AND ITS BOSE CONDENSATION

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### ABSTRACT

The three optical responses of excitonic molecule; giant two-photon absorption, luminescence and optical conversion from single exciton are theoretically discussed. Then the luminescence spectrum characteristic of Bose-condensed excitonic molecules is presented by taking account of the final state interaction between the excitonic molecule and the single exciton at the finite system temperature. Lastly is answered a question whether the third order optical process of the giant two-photon absorption due to the excitonic molecule and its subsequent emission leaving the single exciton behind is considered as two separable processes of absorption and emission or as an inseparable process like two-photon Raman scattering.

### I. INTRODUCTION

The excitonic molecule<sup>1)</sup> is the bound state of two single excitons and its internal motion is visualized in analogy to a hydrogen molecule, the positive holes playing the role of the protons. However, this excitonic molecule has two prominent characters in contrast with the hydrogen molecule. The first character of the excitonic molecule gas is its large quantum effect as an assembly of Bose-particles, which comes from much lighter translational mass of the excitonic molecule. The Bose-condensation of excitonic molecules may be expected from this character.<sup>2)</sup> The second prominent character comes from the fact that the excitonic molecule gas constitutes the open system in close contact with radiation field. By making the best use of this character, firstly the Bose-condensed system of the excitonic molecules can be created directly through giant two-photon excitation.<sup>3)</sup> Secondly, evidence for Bose-condensation of excitonic molecules can be found in the luminescence

spectrum due to radiative decay of the excitonic molecules.<sup>4)</sup> Thirdly, the Bose-condensed excitonic molecules oscillate with a common phase with respect to the ground state, and the whole system behaves as a macroscopic quadrupole-moment. Therefore it can interact coherently with the coherent radiation field through two-photon transitions.<sup>5)</sup> This point is in a striking contrast with the quantum fluid near the ground state. As an example, self-induced transparency associated with the two-photon transition due to the excitonic molecule may take place.<sup>5)</sup>

Since optical methods are used not only to generate the Bose-condensed system of excitonic molecules but also to experimentally confirm the Bose-condensation, the complete knowledge of electronic structure<sup>6)</sup> and optical properties<sup>7)</sup> of excitonic molecule is required for studying its Bose-condensation. This is discussed in Sec. II. The emission spectrum characteristic of Bose-condensed excitonic molecules<sup>8)</sup> is discussed in Sec. III. As a reflection of the second character, there arises a question whether the third order optical process of two-photon absorption by the excitonic molecule and its subsequent emission leaving behind a single exciton, can be considered as two separable processes of absorption and emission or as an inseparable process of Raman scattering.<sup>9)</sup> This is answered in Sec. IV. Section V is devoted to the conclusion.

## II. OPTICAL PROPERTIES OF EXCITONIC MOLECULES<sup>6,7)</sup>

We have three optical processes relevant to the excitonic molecule; giant two-photon absorption to make the excitonic molecule, luminescence due to radiative decay of the excitonic molecule into a single exciton and optical conversion of an exciton into the excitonic molecule by one photon absorption; the reverse process of the second. Selection rules and several related topics for these optical processes are discussed for CuCl, CuBr and CdS.

## 2-1. Excitonic Molecule in CuCl.

Electronic structure of CuCl crystal is characterized by  $\Gamma_7$  valence band and  $\Gamma_6$  conduction band. Two kinds of excitons with symmetry  $\Gamma_2$  and  $\Gamma_5$  are formed by superposing excitations of a valence electron into the conduction band.  $\Gamma_2$  exciton is optically inactive due to pure triplet spin structure and  $\Gamma_5$  exciton is optically active. State of the excitonic molecule is also described by superposition of excitations of two valence electrons into the conduction band. In semiconductors, the exchange interaction within the same band are important for the formation of the excitonic molecule. Therefore, two-electron state and two-hole state with zero angular momentum, respectively, are a good approximation to compose an excitonic molecule, and the interband electron-hole exchange interaction is taken into account as the perturbation. It is noted that the intra-band hole-hole exchange energy is estimated to be 30 meV and the inter-band electron-hole exchange energy is 3 meV. On the other hand, the lowest state of the excitonic molecule in CuCl is described as a linear combination of two optically active  $\Gamma_5$  and two-optically inactive  $\Gamma_2$  exciton states:

$$|\Gamma_1^{\text{mol}}\rangle\rangle = \frac{1}{\sqrt{V}} e^{i\mathbf{K}\cdot\mathbf{R}_0} \Psi^{++}(r, r', R) |0, 0\rangle\rangle, \quad (2-1)$$

where

$$|0, 0\rangle\rangle = \frac{1}{2} |J_t = 0; (J_{\text{exc}}=0)^2\rangle + \frac{\sqrt{3}}{2} |J_t = 0; (J_{\text{exc}}=1)^2\rangle$$

and  $\Psi^{++}$  describes the internal motion of two holes  $R$  and two pairs of an electron and a hole  $r$  and  $r'$ . This electronic structure in semiconductors gives a hint to the idea of exciting the excitonic molecule directly by two-photon excitation through the optically active part and observing its existence in the luminescence due to its radiative decay into a composing exciton. The next lowest state of the excitonic molecule in CuCl is made in terms of the envelope function which is odd to the exchange of two holes. This sacrifices the hole-hole intra-band

exchange energy. This state, however, is optically forbidden for the following three processes; the two-photon excitation, the luminescence due to the radiative decay into any exciton state and the optical conversion of a single exciton of any kind into this state of the excitonic molecule. The selection rules for these three optical processes are listed in Fig. 1. The second lowest state of the excitonic molecule in

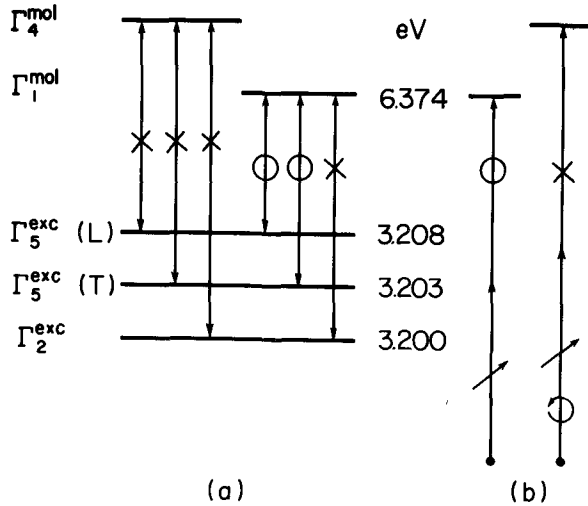


Fig.1. Energy diagram of exciton and excitonic molecule in CuCl. (a) shows the selection rule for the luminescence of excitonic molecule and the optical conversion of an exciton into an excitonic molecule and (b) shows that of the giant two-photon absorption due to excitonic molecule.  $\circ$  and  $\times$  mean the allowed and forbidden transitions, respectively.

CuCl has  $\Gamma_4$  character for the Bloch function part and this is multiplied by the envelope function which is odd with respect to exchange of two holes. The Bloch function part has the finite matrix element for the second order electron-radiation interaction as realized from the fact that  $\Gamma_5 * \Gamma_5 (= \Gamma_1 + \Gamma_3 + \Gamma_4 + \Gamma_5)$  contains  $\Gamma_4$  state. However it vanishes when the integration in the coordinate of hole-hole separation is performed for the final molecular state due to its odd character. The

luminescence from this molecular state and the optical conversion to this molecular state from any exciton state are also forbidden due to the same reason.

## 2-2. Excitonic Molecule in CuBr

In the crystal of CuBr, the bottom of the conduction band has the same symmetry  $\Gamma_6$  as CuCl but the top of the valence band is composed of four-fold degenerate  $\Gamma_8$  state. Two kinds of excitons with total angular momentum  $J_{\text{exc}} = 1$  ( $\Gamma_5$ ) and  $J_{\text{exc}} = 2$  ( $\Gamma_3 + \Gamma_4$ ) are formed from superposition of excitations of a valence electron into the conduction band. An exciton of  $J_{\text{exc}} = 2$  ( $\Gamma_3 + \Gamma_4$ ) has the pure triplet electron-hole spin structure and is optically inactive. In this material also, the electron-electron and the hole-hole intraband exchange energies which are taken into account in the effective mass calculation are much larger than the electron-hole interband exchange energy. Therefore as the basis functions of the excitonic molecule, the zero angular momentum state  $|0,0\rangle_e$  of two electrons is accepted because it minimizes the electron-electron intraband exchange energy, and the  $J_h = 0$  and  $J_h = 2$  states  $|J_h, m_h\rangle_h$  are chosen due to the same reason from four states  $J_h = 0, 1, 2$  and  $3$  which are made from two  $j = 3/2$  holes. The basis functions for the low lying states of an excitonic molecule with the total angular momentum  $J_t = 0$  and  $2$ , are given by

$$|J_t, m_t\rangle\rangle = |0,0\rangle_e \cdot |J_h, m_h\rangle_h \quad (J_t = 0, 2 \text{ and } J_h = 0, 2). \quad (2-2)$$

The state of the excitonic molecule is described in terms of these basis functions and the envelope function of the internal motion  $\Psi$  as follows;

$$|\Gamma^{\text{mol}}(J_t, m_t)\rangle\rangle = \frac{1}{\sqrt{V}} e^{i\mathbf{K}\cdot\mathbf{R}0} \Psi^{++}(\mathbf{r}, \mathbf{r}', \mathbf{R}) |J_t, m_t\rangle\rangle. \quad (2-3)$$

The molecular state  $|0,0\rangle\rangle$  is decomposed into two parts which are made from basis functions of two  $\Gamma_5$  ( $J_{\text{exc}} = 1$ ) excitons and two  $\Gamma_3 + \Gamma_4$  ( $J_{\text{exc}} = 2$ ) excitons as follows;

$$|0,0\rangle\rangle = \sqrt{\frac{2}{8}} |0,0: (J_{\text{exc}}=1)^2\rangle + \sqrt{\frac{5}{8}} |0,0: (J_{\text{exc}}=2)^2\rangle . \quad (2-4)$$

On the other hand, the molecular state of  $|2, m_t\rangle\rangle$  is divided into three parts of  $(J_{\text{exc}} = 1)^2$ ,  $(J_{\text{exc}} = 1) \times (J_{\text{exc}} = 2)$  and  $(J_{\text{exc}} = 2)^2$ . Because of this cross term, the  $J_{\text{exc}} = 2$  excitonic molecule can radiate by annihilating a  $J_{\text{exc}} = 1$  exciton radiatively and leaving a spin triplet exciton  $J_{\text{exc}} = 2$ . The components of  $J_{\text{exc}} = 1$  in  $|2, m_t\rangle\rangle$  are equal to each other for all  $m_t = \pm 2, \pm 1, 0$  as well as equal to that of  $|0,0\rangle\rangle$  and therefore these states have the same value of the electron-hole exchange energy  $3/4 \Delta_{\text{exc}}^{\text{exch}}$ . Here the internal motion of an exciton is assumed not to be modified in the excitonic molecule and  $\Delta_{\text{exc}}^{\text{exch}}$  is the energy splitting of  $J_{\text{exc}} = 1$  and 2 excitons due to the electron-hole exchange interaction. The interband matrix elements of hole-hole Coulomb interaction<sup>6,7)</sup> are expressed by three parameters  $\Delta, \Delta'$  and  $\Delta''$  as the perturbations on the solutions obtained by the effective mass theory. When these interactions are taken into account, the energy spectrum of an excitonic molecule in CuBr is given as follows;<sup>6,7)</sup>

$$\begin{aligned} E_{\text{mol}}(\Gamma_1) &= \Delta + 2\Delta' + \Delta'' \\ E_{\text{mol}}(\Gamma_3) &= \Delta + \Delta'' \\ E_{\text{mol}}(\Gamma_5) &= \Delta - \Delta'' , \end{aligned} \quad (2-5)$$

where the energy reference is taken at  $2\varepsilon_{1s} - E_{\text{mol}}^b + 3/4\Delta_{\text{exc}}^{\text{exch}}$ .

The selection rules of these three optical processes relevant to the excitonic molecule in CuBr are listed in Fig.2. Giant two-photon absorption due to the excitonic molecule shows dependence of its intensity on the polarization of exciting light as shown in Table 1. Here the direction of the light propagation is taken in the z-axis of the crystal and the polarization of the light makes an angle  $\phi$  against the y-axis in the x-y plane. It is noted that the three levels show different angular dependence in the giant two-photon absorption for linearly polarized light. On the other hand,  $\Gamma_1$  excitonic molecule is

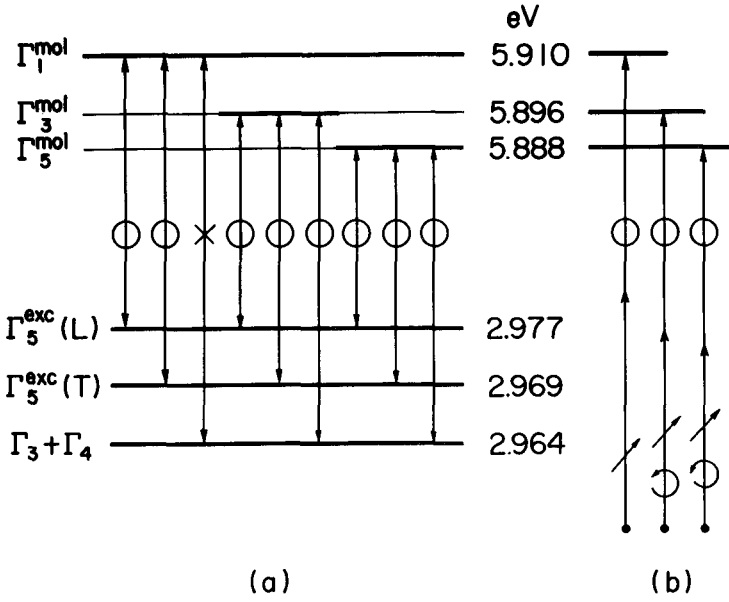


Fig.2. Energy diagram of exciton and excitonic molecule in CuBr. (a) shows the selection rule for the luminescence and the optical conversion of an exciton into an excitonic molecule and (b) shows that of the giant two-photon transition of an excitonic molecule.

| Molecule   | $E_{mol}/2$ in eV | relative absorption intensity |               |
|------------|-------------------|-------------------------------|---------------|
|            |                   | linear pol.                   | circular pol. |
| $\Gamma_1$ | 2.955             | 4                             | 0             |
| $\Gamma_3$ | 2.948             | $6\sin^2 2\phi$               | 1             |
| $\Gamma_5$ | 2.944             | $6\cos^2 2\phi + 1$           | 1             |

Table 1. Giant two-photon absorption due to excitonic molecule in CuBr. The direction of the light propagation is taken in the z-axis of the crystal and the polarization of the light makes an angle  $\phi$  against the y-axis in the x-y plane.

forbidden and  $\Gamma_3$  and  $\Gamma_5$  are allowed with equal intensity in the giant two-photon absorption for circularly polarized lights.

## 2-3. Excitonic Molecule in CdS

The bottom of the conduction band and the top of the valence band are described by  $\Gamma_7$  and  $\Gamma_9$  states, respectively. The lowest excitonic and molecular states are constructed from properly symmetrized electron functions  $\Gamma_7$  and hole functions  $\Gamma_9$ . Optically active  $\Gamma_5$  exciton and inactive  $\Gamma_6$  exciton of pure spin triplet are formed, and the ground state of the excitonic molecule is described in terms of the exciton basis functions as follows,<sup>6,7)</sup>

$$|\Gamma_1^{\text{mol}}\rangle = \frac{1}{\sqrt{V}} e^{i\mathbf{K}\cdot\mathbf{R}_0} \Psi^{++}(\mathbf{r}, \mathbf{r}', \mathbf{R}) |\Gamma_1\rangle \quad (2-6)$$

with

$$\begin{aligned} |\Gamma_1\rangle = & \frac{1}{2} [ |\Gamma_{5x}\rangle + |\Gamma_{5x}\rangle - |\Gamma_{5y}\rangle + |\Gamma_{5y}\rangle \\ & + |\Gamma_{6-}\rangle + |\Gamma_{6-}\rangle - |\Gamma_{6+}\rangle + |\Gamma_{6+}\rangle ] \quad (2-7) \end{aligned}$$

where (  $|\Gamma_{5x}\rangle$  ,  $|\Gamma_{5y}\rangle$  ) =  $\frac{1}{\sqrt{2}} [ \pm |P_1^1\rangle - |P_1^{-1}\rangle ]$  are optically active to the light with polarization in x- and y-directions, respectively, and  $|\Gamma_{6\pm}\rangle = \frac{1}{\sqrt{2}} [ |P_2^2\rangle \pm |P_2^{-2}\rangle ]$  are optically inactive excitons with pure triplet spin structure. The selection rules are listed in Fig. 3.

When the uniaxial field ( $\sigma$ ) of the stress is applied perpendicular to the c-axis and the x-direction is chosen in this field, the  $\Gamma_5$  exciton is split into two components  $\Gamma_{5x}$  ( $E \parallel \sigma$ ) and  $\Gamma_{5y}$  ( $E \perp \sigma$ ) with polarization in the x- and y-axis, respectively. On the other hand, the emission line due to decay of the excitonic molecule splits also into two lines under the uniaxial stress perpendicular to the c-axis, but the polarization characteristics are reversed.<sup>10)</sup> This can be understood in terms of eq. (2-6) as follows: When one  $\Gamma_{5x}$  (or  $\Gamma_{5y}$ ) exciton is radiatively annihilated in the radiative decay of the excitonic molecule, the other  $\Gamma_{5x}$  (or  $\Gamma_{5y}$ ) exciton should remain according to eq. (2-6). Therefore the  $E \parallel \sigma$  and  $E \perp \sigma$  polarized lights



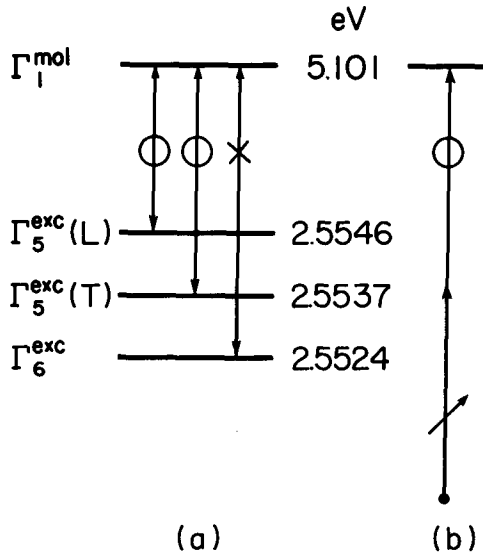


Fig.3. Energy diagram of exciton and excitonic molecule in CdS. (a) shows the selection rule for the luminescence and the optical conversion of an exciton into an excitonic molecule and (b) shows that of giant two-photon absorption due to an excitonic molecule.

should be observed at  $h\nu_{\parallel}(\Gamma_{5x}) = E_{\text{mol}} - E_{\text{exc}}(\Gamma_{5x})$  and  $h\nu_{\perp}(\Gamma_{5y}) = E_{\text{mol}} - E_{\text{exc}}(\Gamma_{5y})$ , respectively. Therefore, the reversed characteristics of the polarization between the reflection spectrum due to excitons and the emission spectrum of the M-line can be explained. On the other hand, the bound exciton should not split as observed in the same reference.<sup>10)</sup> As a result, this experiment gave a strong support of the M-line to the radiative decay of the excitonic molecule in CdS and ZnO.

### III. EMISSION SPECTRUM FROM BOSE-CONDENSED EXCITONIC MOLECULES<sup>4,8)</sup>

The excitonic molecules can be accumulated at high density by the giant two-photon excitation discussed in the preceding section. These excitonic molecules are expected to show the Bose-condensed state from the large quantum effect as Bose particles. On the other hand, the

excitonic molecules with any value of the translational momentum are radiative through the process of annihilating one electron-hole pair radiatively and leaving the other pair as a free exciton. As a result, detailed information about the state of the excitonic molecule gas, *e.g.*, evidence of its Bose-condensation, can be obtained very clearly from the emission spectrum.

In this section, the characteristic emission spectrum is calculated for the Bose-condensed system of the excitonic molecules at finite temperature. Here we take into account the effect on the emission spectrum due to the final state interaction between the excitonic molecule which has been radiatively annihilated and the single exciton created in this emission process.

The emission spectrum in the linear response is given, apart from the unimportant factor, by

$$I(\omega) = 2\pi \sum_{i,f} |\langle f | p | i \rangle|^2 e^{-\beta E_i} \delta(\omega + E_f - E_i), \quad (3-1)$$

where  $p = g \sum_K a_K^+ b_K$  is the dipole moment operator corresponding to the radiative annihilation of an excitonic molecule ( $b_K$ ) with leaving a single exciton ( $a_K^+$ ), and  $\hbar\omega$  is the energy of the emitted photon. Here  $I(\omega)$  is expressed in terms of the response function  $\chi(i\omega_n)$  as follows;

$$I(\omega) = 2g^2 n(\bar{\omega}) \text{Im} [\chi(i\omega_n) |_{\bar{\omega} + i\delta}], \quad (3-2)$$

and  $\chi(i\omega_n)$  is defined by  $\chi(i\omega_n) \equiv \frac{1}{2} \int_{-\beta}^{\beta} d\tau e^{i\omega_n \tau} \chi(\tau)$ , and

$$\chi(\tau) = \sum_{K,K'} \langle T_{\tau} a_K^+(\tau) b_K(\tau) b_{K'}^+ a_{K'} \rangle,$$

where  $\omega_n = 2\pi n/\beta$  and  $\beta = 1/kT$ ,  $\bar{\omega} = \omega + \mu_{\text{exc}} - \mu_{\text{mol}}$  (the photon energy is measured from the chemical potential difference ( $\mu_{\text{mol}} - \mu_{\text{exc}}$ ) of the excitonic molecule and the exciton) and  $n(\bar{\omega})$  is the boson distribution function. The contribution to the response function from the Bose-

condensed excitonic molecules as well as from the molecules with the finite momentum are drawn in Fig. 4. Firstly, the final state

$$\begin{aligned} \chi &= \text{Diagram 1} + \text{Diagram 2} \\ \triangle &= \text{Diagram 3} + \text{Diagram 4} + \text{Diagram 5} \\ \triangle &= \text{Diagram 6} + \text{Diagram 7} + \text{Diagram 8} \end{aligned}$$

Fig.4. Response function corresponding to the emission of Bose-condensed excitonic molecule (the first term) and of the excitonic molecule in the finite momentum state (the second term). The white circle describes the electron-radiation interaction and the triangle is the electron-radiation interaction modified by the final state interaction. The shaded part represents the repeated scattering between the exciton and the excitonic molecule.

Fig.5. The final state interaction between the excitonic molecule and the exciton is taken into account by the coupled Dyson equations.

interaction between the single exciton and the excitonic molecule is taken into account (1) through the process of exciting the condensed excitonic molecule into the finite momentum state and its reverse process in the response function and (2) by the repeated scattering between the exciton and the excitonic molecule in the finite momentum state. The first process is evaluated by the vertex correction of the emission process drawn in Fig. 4 and the second effect is calculated by the coupled Dyson equations for four kinds of polarizabilities drawn in Fig. 5. Secondly, the interaction of the optically created exciton with the medium of excitonic molecules is also taken into account (3) by replacing the bare interaction  $V$  working between the exciton and one of the excitonic molecules by the renormalized  $t$ -matrix  $V^*$  described in Fig. 6 in the expression of the response function  $\chi(z)$  and in solving the coupled Dyson equations in Fig. 5 and (4) by the self-energy of the exciton due to interactions with the condensed excitonic molecules described in Fig. 7. The medium of the excitonic molecules is assumed to be described in the framework of the Bogoliubov approximation in terms of the  $t$ -matrix  $W$  between two excitonic molecules in the crystal vacuum. Then the response function  $\chi(z)$  is described in terms of  $V^*$  and  $W$  as well as four kinds of polarizabilities  $P_i(z)$  ( $i = 1, 2, 3$  and  $4$ ) where

$$P_i(z) = \frac{1}{\beta} \sum_n G_i(z) G_{\text{exc}}(z - i\omega_n)$$

$$\text{and } G_1(z') = G_2(z') = \frac{u_p^2}{z' - \omega_p} - \frac{v_p^2}{z' + \omega_p} \text{ and } G_3(z') = G_4(z') = -u_p v_p$$

$\times \left\{ \frac{1}{z' - \omega_p} - \frac{1}{z' + \omega_p} \right\}$  are the Green functions of the excitonic molecule

and  $G_{\text{exc}}$  is one of the single exciton with the self-energy described by

$$\text{Fig. 7. Here } u_p^2 = \frac{p^2/2M + n_0W + \omega_p}{2\omega_p}, \quad v_p^2 = \frac{p^2/2M + n_0W - \omega_p}{2\omega_p}, \quad \omega_p^2 = \frac{p^2}{M} \times n_0W + \frac{p^4}{4M^2}.$$

The emission spectrum of eq. (3-2) is evaluated for several values

$$V^* = \bullet + \text{[diagram: semi-circular loop with arrows]} + \text{[diagram: two semi-circular loops with arrows]} + \dots$$

Fig.6. The interaction of the single exciton with the medium of Bose-condensed system of excitonic molecules is taken into account by replacing  $V$  by the  $t$ -matrix  $V^*$  due to the repeated scattering with one of the excitonic molecules.

$$\Sigma = \text{[diagram: dashed lines forming a loop]} + \text{[diagram: dashed lines with a shaded semi-circular loop]} + \text{[diagram: dashed lines with two shaded semi-circular loops]} + \dots$$

Fig.7. The self-energy of the single exciton due to the interaction with the condensed excitonic molecules.

of molecular concentrations and system temperatures in which the Bogoliubov approximation is justified. Here the photon energy  $\hbar\omega$  is normalized by  $\hbar^2/Mf_0^2$ , where  $f_0$  is the scattering length which is related to  $W$  by  $W = 4\pi\hbar^2 f_0/M$ , and  $V^*/W$  is taken as a constant parameter. The emission spectra are drawn in Fig. 8 for several values of  $V^*/W$  and of concentrations of the excitonic molecules.

Some of the interesting results are listed:

- (1) The sharp emission line due to the radiative decay of Bose-condensed excitonic molecules is somewhat broadened due to scattering of the exciton in the final state with the medium of the Bose-condensed excitonic molecules. The width of this sharp line depends on the concentration of the excitonic molecules and the system temperature as shown in Fig. 8. Note the order change of the abscissa of the photon energy in Fig. 8.
- (2) The side band appears in the lower energy side due to the two origins; (a) the radiative decay of a Bose-condensed excitonic molecule accompanied with excitation of the individual and collective motions of the excitonic molecules and (b) the radiative decay of the excitonic molecules with the finite momentum. Both contributions are described by the second process of Fig. 4 but a part of this side band intensity is transferred into the sharp line through the final state interaction described by the vertex correction in the first process of Fig. 4.
- (3) The emission singularity appears at  $\hbar\omega = (2-\sqrt{3})n_0W$  due to the van Hove singularity of the joint state density of the excitonic molecule

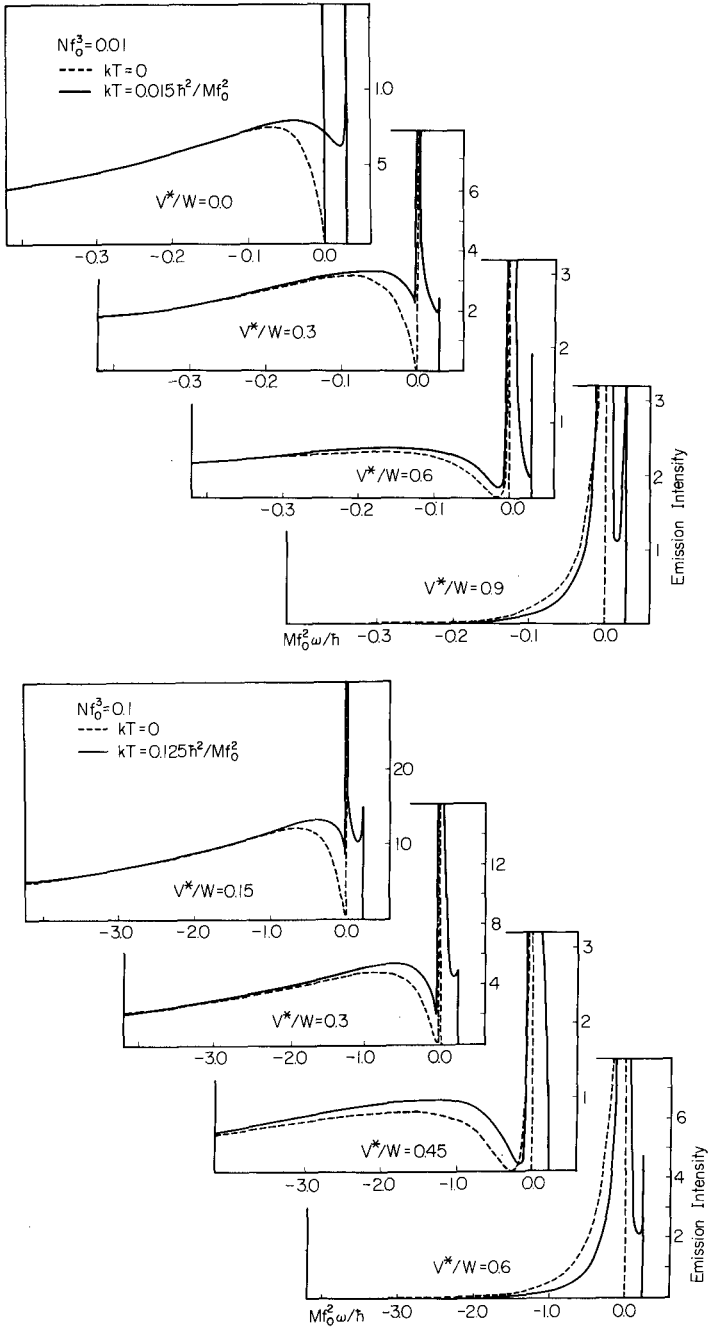


Fig.8. The emission spectra characteristic of the Bose-condensed excitonic molecules are shown for various values of the system temperature and the concentration with parameters  $V^*/W$ .

and the single exciton. However it will be smeared or weakened when the finite value of the momentum of the emitted light is taken into

account.

(4) At the lower concentration of the total excitonic molecules than the case of Fig. 8, the ratio of the sharp line intensity to the total area is very close to unity and it decreases with the increase of the total concentration and the rise of the system temperature as shown in Fig. 8.

(5) As the parameter  $V^*/W$  is varied, the profile of the emission spectrum is changed very much around  $V^*/W = 0.5$ . The curve in Fig. 8 can fit the observed emission spectra<sup>11)</sup> for a wide range of concentrations with respect to the position and the profile of the sharp line and the band width and the profile of the side band besides the lower energy tail. The theoretical curve has a rather longer tail. The side band peak is located at the photon energy shifted by an order of magnitude of  $n_0 W$  below the sharp peak.  $n_0$  is approximately proportional to the total concentration  $n$  of the excitonic molecules and therefore the side band is observable only in the case of high density excitation of the excitonic molecules under the present experimental resolution in the emission spectrum. When the exciton mass  $M/2$  is  $0.4 m + 4.2 m$  and the scattering length  $f_0$  is estimated to be  $4a_0$  ( $a_0$  is the exciton Bohr radius and  $7\text{\AA}$  for CuCl), the peak separation of the side band from the sharp line is evaluated to be  $1.6 \text{ meV}$  for  $nf_0^3 = 0.1$  ( $n = 5 \times 10^{18}/\text{cc}$ ) and  $0.2 \text{ meV}$  for  $nf_0^3 = 0.01$  ( $n = 5 \times 10^{17}/\text{cc}$ ).

#### IV. LUMINESCENCE OR RAMAN SCATTERING?

By using the second character of excitonic molecules, the Bose-condensed system of excitonic molecules can be directly created by the giant two-photon absorption and the evidence of Bose-condensation can be observed in the characteristic emission spectrum of excitonic molecules. On the other hand, here arises a question whether the third order optical process of two-photon absorption due to the excitonic molecule and its subsequent emission, leaving a single exciton behind,

can be considered as two separable processes of absorption and emission or an inseparable process like Raman scattering.

To answer this question, the transition rate of this third order optical process is evaluated in terms of the damping theory for the interaction of the excitonic molecule in the intermediate state and the single exciton in the final state with their surrounding reservoir. The initial state is composed of the ground state and the radiation field  $(n_1, n_2)$  for the incoming light of frequency  $\omega_1$  and the outgoing light of frequency  $\omega_2$ . The intermediate state of an excitonic molecule is connected with the ground state through two-photon transition of frequency  $\omega_1$  by  $V_1^+$  and with the final state of single exciton through one-photon transition of frequency  $\omega_2$  by  $V_2^+$ . Starting from the initial state  $i = (g, n_1, n_2)$  at  $t = 0$ , the probability  $P(t)$  of finding the final state  $f = (m, n_1-2, n_2+1)$  at time  $t$  is given by

$$\begin{aligned}
 P(t) = & \int_0^t dt_1 \int_0^{t_1} dt_2 \int_0^{t_2} dt_3 \int_0^t dt'_1 \int_0^{t'_1} dt'_2 \int_0^{t'_2} dt'_3 \text{Tr}_R \\
 & \cdot \langle f | e^{-i(t-t'_1)H} V_2^+ e^{-i(t'_1-t'_2)H} V_1 e^{-i(t'_2-t'_3)H} V_1 e^{-it'_3H} \\
 & \cdot \rho_0(H) e^{it_3H} V_2 e^{i(t_2-t_3)H} V_1^+ e^{i(t_1-t_2)H} V_1^+ e^{i(t-t_1)H} | f \rangle .
 \end{aligned} \tag{4-1}$$

Here  $\text{Tr}_R$  describes taking the trace over the coordinates of the surrounding reservoir and  $\rho_0(H)$  is the distribution function of the total system. The process of two-photon absorption due to the excitonic molecule is assumed to be completed instantaneously because  $\omega_1$  is enough off-resonant to an exciton level. Then we have three kinds of time orderings for the contribution to  $P(t)$  as shown in Fig. 9. The first contribution is expressed as follows;

$$\begin{aligned}
 P_i(T) = & 2\text{Re} \int_0^t dt_1 \int_0^{t_1} dt_2 \int_0^{t_2} dt_3 \int_0^{t_3} dt'_1 \int_0^{t'_1} dt'_2 \int_0^{t'_2} dt'_3 \\
 & \cdot \text{Tr}_R \langle f | \{ e^{-i(t_1-t_2)H} \left[ \left[ e^{-i(t_2-t_3)H} \left[ e^{-i(t_3-t'_1)H} (V_2^+)_{c'c} \right. \right. \right.
 \end{aligned}$$



$$\begin{aligned}
& \cdot \left\{ e^{-i(t'_1-t'_2)H} (V_1)_{b'b} e^{-i(t'_2-t'_3)H} (V_1)_{a'a} \rho_0 e^{i(t'_2-t'_3)H} \right\}_0 \\
& \cdot e^{i(t'_1-t'_2)H} \left. \right\}_n e^{i(t'_3-t'_1)H} \left. \right] (V_1^+)_{d'd} e^{i(t'_2-t'_3)H} \left. \right] (V_1^+)_{e'e} \\
& \cdot e^{i(t'_1-t'_2)H} \left. \right\} (V_2)_{f'f} |f\rangle e^{i\omega_1(t'_2+t'_3-t'_2-t'_3)} e^{-i\omega_2(t'_1-t'_1)} \\
& \hspace{15em} (4-2)
\end{aligned}$$

$$= 2t \operatorname{Re} \int_0^\infty \int_0^\infty d\tau_3 d\tau_2 d\tau_1 \Sigma \ll ff' | \hat{U}(\tau_3) | \rho e \gg$$

$$\ll md' | \hat{U}(\tau_2) | c'n \gg \ll cn | \hat{U}(\tau_1) | b'o \gg \rho_{aa} e^{-i\omega_2\tau_3} e^{i2\omega_1\tau_1}$$

$$e^{i(2\omega_1-\omega_2)\tau_2} (V_2^+)_{c'c} (W_1)_{b'a} (W_1^+)_{d'c} (V_2)_{f'f}, \quad (4-3)$$

where  $(W_1)_{b'a} \equiv i(V_1)_{b'b}(V_1)_{a'a}/(\omega_{a'a}-\omega_1)$  is the two-photon transition matrix element via the intermediate exciton state and  $(W_1)_{b'a}$  and  $(W_1^+)_{d'c}$  are obtained after integrations with respect to  $\tau' = t'_2 - t'_3$

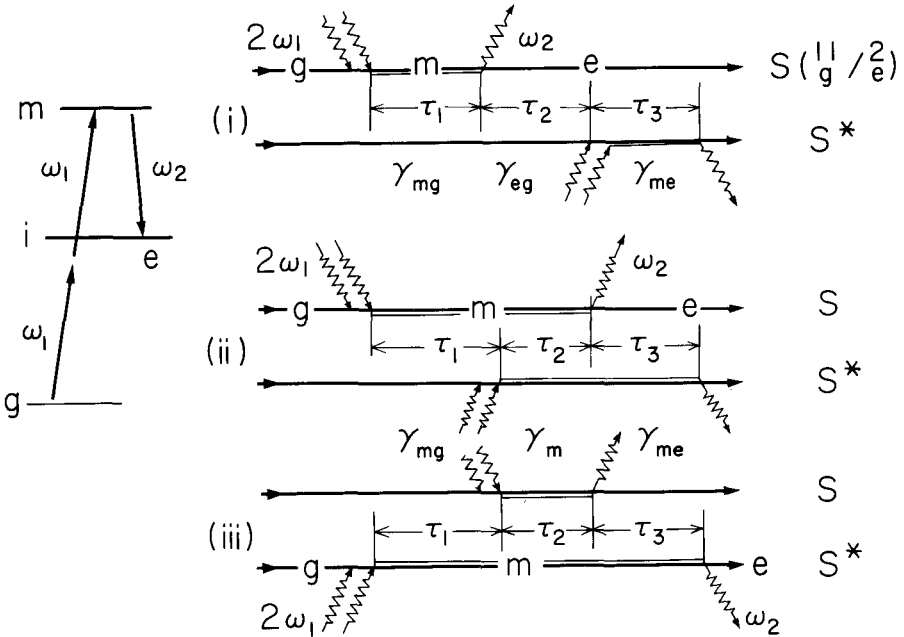


Fig.9. The third order optical process is composed of three types of contributions which depend on time orderings of the interaction with the radiation field.

and  $\tau = t_2 - t_3$ . Here the damping theory is used to take into account the effect of the surrounding reservoir as follows;

$$\begin{aligned} \langle\langle ab | \hat{U}(\tau) | cd \rangle\rangle &\equiv \{ \langle a | e^{-iH\tau} | c \rangle \langle d | e^{iH\tau} | b \rangle \}_{av} \\ &= \delta_{ac} \delta_{db} e^{-i\omega_{ab}\tau - \Phi_{ab}\tau}, \end{aligned} \quad (4-4)$$

where  $\Phi_{ab} = \Phi_{ba}^* = \gamma_{ab} + i\Delta_{ab}$

$$\gamma_{ab} = \gamma_{ab}^c + \frac{1}{2}(\Gamma_a + \Gamma_b)$$

$$\Phi_{aa} = \gamma_a = \gamma_a^c + \Gamma_a. \quad (4-5)$$

$(1/\Gamma_a)$  is the life-time of level a,  $\gamma_a^c$  is the inelastic collision frequency of level a and  $\gamma_{ab}^c$  is composed of the elastic as well as inelastic collisions of levels a and b. By a similar way, the second and third contributions of diagrams (ii) and (iii) are evaluated as follows;

$$\begin{aligned} P_{ii}(t) &= 2t \operatorname{Re} \int_0^\infty \int_0^\infty \int_0^\infty d\tau_3 d\tau_2 d\tau_1 \Sigma \rho_{aa} \langle\langle ff' | \hat{U}(\tau_3) | c'0 \rangle\rangle \\ &\quad \cdot \langle\langle c0 | \hat{U}(\tau_2) | \ell e \rangle\rangle \langle\langle md' | \hat{U}(\tau_1) | b'n \rangle\rangle \\ &\quad \cdot (V_2^+)_{c'c} (W_1)_{b'a} (W_1^+)_{d'e} (V_2)_{f'f} e^{2i\omega_1\tau_1} e^{-i\omega_2\tau_3} \end{aligned} \quad (4-6)$$

$$\begin{aligned} P_{iii}(t) &= 2t \operatorname{Re} \int_0^\infty \int_0^\infty \int_0^\infty d\tau_3 d\tau_2 d\tau_1 \Sigma \langle\langle ff' | \hat{U}(\tau_3) | c'0 \rangle\rangle \\ &\quad \cdot \langle\langle c0 | \hat{U}(\tau_2) | b'n \rangle\rangle \langle\langle am | \hat{U}(\tau_1) | \ell e \rangle\rangle \\ &\quad \cdot \rho_{d'd'} (V_2^+)_{b'b} (W_1)_{b'a} (W_1^+)_{d'e} (V_2)_{f'f} e^{-2i\omega_1\tau_1 - i\omega_2\tau_3}. \end{aligned} \quad (4-7)$$

The expression of eq.(4-4) is inserted into eqs.(4-3), (4-6) and (4-7) and time integrals are performed. Then the transition rate representing the output of  $\omega_2$ -photon for an influx of  $\omega_2$  photon is

described finally as follows;

$$\begin{aligned}
 F(2\omega_1, \omega_2) &= \lim_{t \rightarrow \infty} P(t)/t \\
 &= A \frac{\gamma_{mg}}{(2\omega_1 - \omega_{mg})^2 + \gamma_{mg}^2} \cdot \frac{\gamma_{me}}{(\omega_2 - \omega_{me})^2 + \gamma_{me}^2} \left[ \frac{2}{\gamma_m} \right. \\
 &+ \frac{\gamma_{eg} \{ 1 + (2\omega_1 - \omega_{mg})(\omega_2 - \omega_{me}) / \gamma_{mg} \gamma_{me} \}}{(2\omega_1 - \omega_2 - \omega_{eg})^2 + \gamma_{eg}^2} \\
 &- \left. \frac{(2\omega_1 - \omega_2 - \omega_{eg}) \{ (2\omega_1 - \omega_{mg}) / \gamma_{mg} - (\omega_2 - \omega_{me}) / \gamma_{me} \}}{(2\omega_1 - \omega_2 - \omega_{eg})^2 + \gamma_{eg}^2} \right] \quad (4-8)
 \end{aligned}$$

where  $A \equiv n_1(n_1-1)(n_2+1) | (W_1)_{mg} |^2 | (V_2)_{me} |^2$ .

In the first process, the difference of phase modulations between the molecule state and the ground state, between the final exciton state and the ground state and between the final exciton state and the molecule state work in the time intervals  $\tau_1$ ,  $\tau_2$  and  $\tau_3$ , respectively. This gives the second and third terms in the bracketed passage of eq. (4-8). On the other hand, in the second and third processes, the excitonic molecule is really created in the time interval  $\tau_2$  and only the radiative damping works in this time interval. Both phase modulation and radiative damping work in other time intervals. These two processes give the first term in the bracketed passage in eq. (4-8). The first process contains the Raman scattering term and the second and third processes give the luminescence terms. The first term is called luminescence type because the frequency  $\omega_2$  of the emission peak is independent of the frequency  $\omega_1$  of the incoming laser light and the second and third terms are of Raman type in the sense that  $\omega_2$  is correlated with  $\omega_1$  as shown in this expression. Let us discuss the following two limiting cases. In the first case, only the molecular state is strongly modulated, which is described by the inequalities:

(a)  $\gamma_{mg} \approx \gamma_{me} = \bar{\gamma} \gg 2\gamma_{eg} > \gamma_m$ . The  $i$ -th contribution, i.e., the second and third terms in the bracketed passage are simplified into the

following two terms:  $\pi\delta(2\omega_1 - \omega_2 - \omega_{eg}) \{ (2\omega_1 - \omega_{mg})^2 + \bar{\gamma}^2 \}$  and  $-\bar{\gamma}$ , respectively. When the spectral width of the incoming laser light is much wider than  $\bar{\gamma}$ , the emitted spectrum is given by integrating  $F(2\omega_1, \omega_2)$  with respect to  $\omega_1$ , which is denoted as  $F(\omega_2)$ . The  $i$ -th contribution is cancelled out each other and the only luminescence part remains finite:  $F(\omega_2) = \pi A(2\bar{\gamma}/\gamma_m) f(\omega_2 - \omega_{me}, \bar{\gamma})$ , where  $f(x, y) = x/(x^2 + y^2)$ . In the second case, the phase only of final exciton state is strongly modulated, which is described by the following inequalities: (b)  $\gamma_{eg} \simeq \gamma_{me} \equiv \bar{\gamma} \gg 2\gamma_{mg} > \gamma_m$ . When the spectral width of the incoming laser light is much larger than  $\bar{\gamma}$ , two components of emitted lights are given by the following equations:  $F(\omega_2) = \pi A f(\omega_2 - \omega_{me}, \bar{\gamma}) [ \bar{\gamma} f(\omega_2 - \omega_{me}, \bar{\gamma}) + 2\bar{\gamma}/\gamma_m ]$ . Therefore the peaks of two emission components are coincident with each other and the integrated intensity has the ratio 1 to  $4\bar{\gamma}/\gamma_m$ . As a result, the luminescence component is dominating as far as the radiative damping  $\gamma_m$  is much smaller than the phase modulation of the exciton in the final state. The emission peak was observed to be independent of the peak frequency of the incoming laser light as far as the spectrum of the laser light covers the excitation frequency of the excitonic molecule.

When the monochromatic laser light is used, the more information is obtained. Then the Raman and luminescence components show the different  $\omega_1$  and  $\omega_2$  dependences and the detailed analysis of experimental data on the basis of eq. (4-8) gives us information of the relaxation times and the radiative life-time of the excitonic molecule as well as their change due to Bose-condensation. In Fig. 10, some examples of emission spectra are shown for various values of  $\omega_1$  with parameters of  $\bar{\gamma}/\gamma_{eg}$  and  $\bar{\gamma}/\gamma_m$ . With increasing the value of  $\bar{\gamma}/\gamma_m$ , the luminescence component is shown to be overcoming the Raman component, although the latter is still observable due to the sharpness of the Raman spectrum.

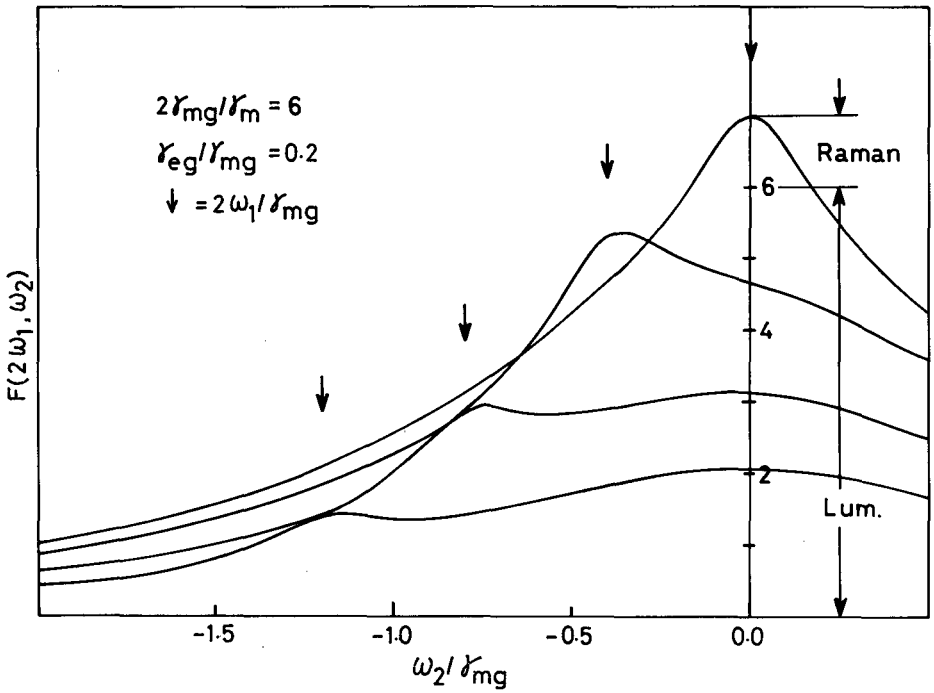
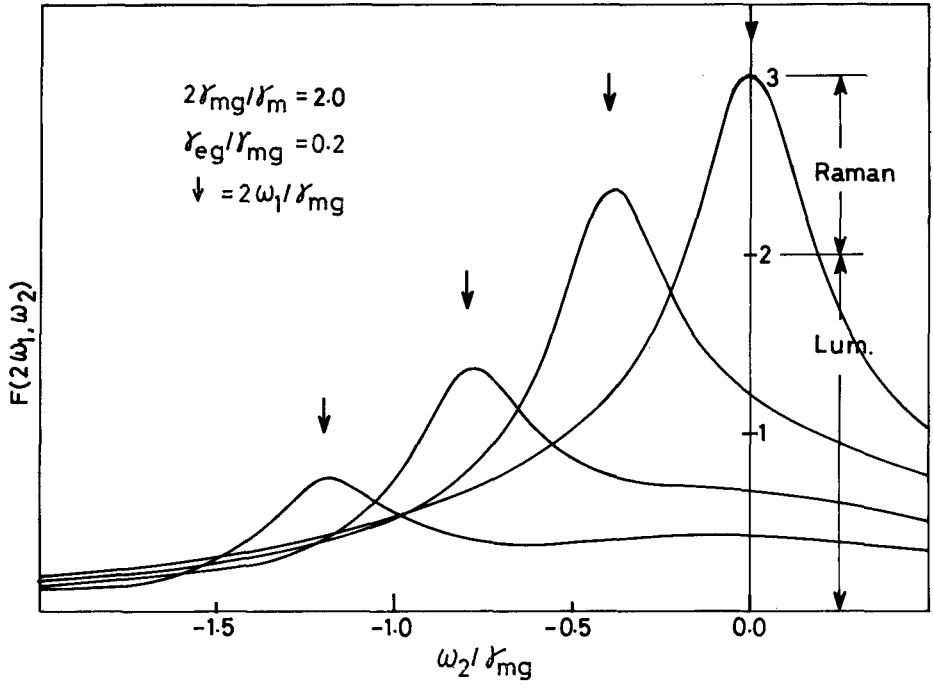


Fig.10. (See next page.)

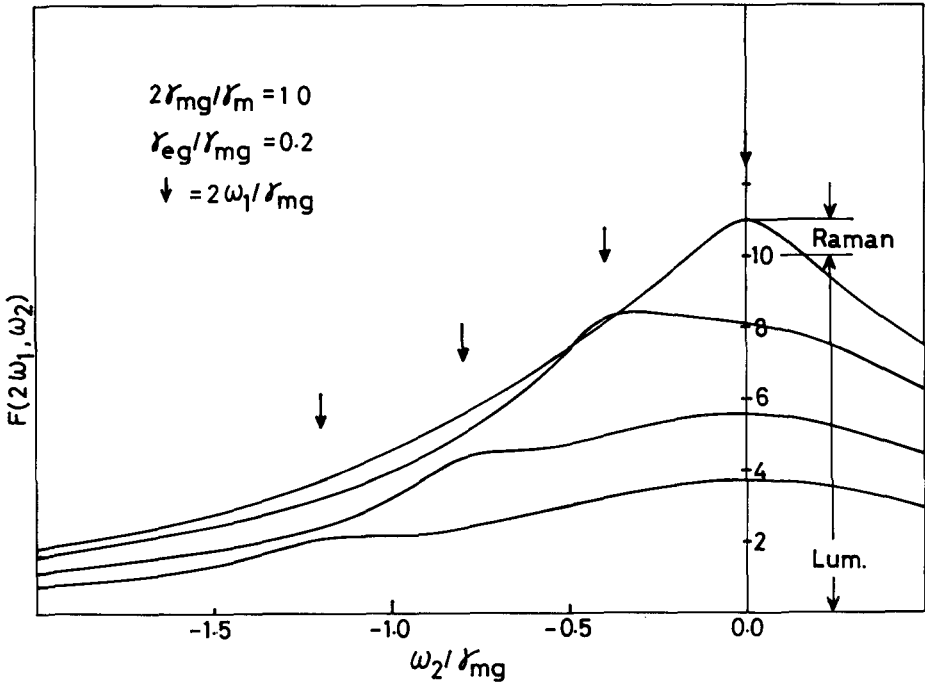


Fig.10. The emission spectra are composed of the luminescence and Raman contributions. As  $\gamma/\gamma_m$  increases, the luminescence part overcomes the Raman part.

## V. CONCLUSION

The giant two-photon absorption due to excitonic molecules have been observed in CuCl,<sup>11)</sup> CuBr<sup>11)</sup> and CdS and the existence of the excitonic molecule was confirmed in these materials. Furthermore the study of the Bose-condensation of excitonic molecules was made possible by the direct excitation of excitonic molecules through the giant two-photon excitation. As discussed in Luminescence Conference<sup>12)</sup> and introduced by Ueta,<sup>13)</sup> we may conclude that the evidence of the Bose-condensation of excitonic molecules was found in the following two experimental facts: First, the sharp emission line and its characteristic side band were observed in CuCl and CuBr under the giant two-photon excitation of excitonic molecules in agreement with theoretical expectations with respects to the position and the profile of the sharp line

and the separation of the side band peak from the sharp line and the profile of the side band, and second, the relative intensity of the sharp line to the total spectral area was observed to decrease with the rise of molecular concentration and the system temperature in agreement at least qualitatively with theoretical expectation.

Finally the following three points will become important in the near future to study the Bose-condensation of the excitonic molecules in more detail. First, the analysis of Raman and luminescence components will give us the information on the relaxation process of the excitonic molecules and the exciton and its change due to the Bose-condensation. Second, the time analyzed emission spectrum of the excitonic molecules will be interesting under the giant two-photon excitation by the picosecond laser pulse. This will make clear the dynamical mechanism of the Bose-condensation and its breaking process due to the relaxation and damping process. The third point is the most interesting. The coherent property of Bose-condensed excitonic molecules is most clearly reflected on the coherent interaction with the coherent radiation field.<sup>5)</sup> Therefore the observation of the coherent optical process relevant to the Bose-condensation such as the self-induced transparency of two-photon transition due to excitonic molecules will bring about more direct and clear evidence for the Bose-condensation of excitonic molecules.<sup>5)</sup>

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