PHYSICAL REVIEW B VOLUME 48, NUMBER 4 15 JULY 1993-II

Brief Reports

Brief Reports are accounts of completed research which, while meeting the usual **Physical Review** *standards of scientific quality, do not warrant regular articles. A Brief Report may be no longer than four printed pages and must be accompanied by an abstract. The same publication schedule as for regular articles is followed, and page proofs are sent to authors.*

Superradiance of interacting Frenkel excitons in a linear system

Yoshihiro Manabe, Tetsuji Tokihiro, and Eiichi Hanamura
Department of Applied Physics, University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113, Japan

(Received 1 December 1992)

A superradiant master equation is solved for a system of fully excited Frenkel excitons interacting with each other through their induced static dipole moments. The superradiant pulse profile and time-resolved emission spectrum are evaluated and shown to depend strongly on the ratio of the induced static and the excitonic transition dipole moments.

Since Dicke[1] introduced the concept of superradiance for coherent spontaneous emission of radiation from a highly excited system of two-level atoms, it has been observed from the gas system of molecules[2] and atoms.[3] An excitation can propagate coherently among atoms (molecules) in a crystal due to its translational symmetry and the dipolar interaction of its transition dipole moments. This elementary excitation is called a Frenkel exciton.[4] The question of how the superradiance of Frenkel excitons is modified was answered very recently.[5,6] Here two effects have been found beyond Dicke's superradiance: chirping, i.e., frequency shifting of the light emitted within the superradiant pulse, and the appearance of a slow emission component. While an excitation can propagate coherently through its dipolar interaction of the transition dipole moments in a crystal, this Frenkel exciton is sometimes accompanied by a static dipole moment. In J aggregates of dyes, e.g., pseudoisocyanine halides,[7,8] the dye molecule has an induced static dipole moment relative to the ground state. This excitation can also propagate as a Frenkel exciton through its transition dipole moment. When more than two excitons are excited in this system, they interact with each other through their static dipolar interaction. These excitons can be described by the *XXZ*-spin model. This contains the *XX*0, Ising, and Heisenberg models as limiting cases. We will clarify in this paper the characteristic features of superradiance phenomena from interacting Frenkel excitons in a chain which depend strongly upon the relative magnitude of the induced static dipole moment to the excitonic transition dipole moment.

First we derive the master equation of superradiance for the density operator of Frenkel excitons $\rho(t)$ by following the procedure of Lehmberg[9] and Gross and Haroche[10] and keeping the static dipole moment induced in the excited state:

$$\frac{d\rho}{dt}=-\hat{\Gamma}\rho-i[\Omega_{ex},\rho] , \tag{1a}$$

$$-\hat{\Gamma}\rho\equiv-\frac{\Gamma}{2}[\hat{S}^{+}\hat{S}^{-},\rho]_{+}+\Gamma\hat{S}^{-}\rho\hat{S}^{+} , \tag{1b}$$

where $\hat{S}^{\pm}\equiv\sum_{j=1}^{N}\hat{s}_j^{\pm}$, $\hat{s}_j^{+}(\hat{s}_j^{-})$ is an excitation (deexcitation) operator at the jth molecule, Γ is spontaneous emission rate of a single molecule $\Gamma=8\pi^2d^2/(3\epsilon_0\hbar\lambda^3)$ with a transition dipole moment d and wavelength λ of the emitted light, and $\hbar\Omega_{ex}\equiv H_{ex}$ denotes the Hamiltonian of Frenkel excitons in a linear chain. We consider a system composed of N molecules. This Hamiltonian is written in terms of spin operators $\hat{s}_j^{\pm}$ as follows:

$$H_{ex}=H_0+H_{XXZ} , \tag{2a}$$

$$H_0\equiv\hbar\omega_0\hat{S}^z\equiv\hbar\omega_0\sum_{j=1}^{N}\hat{s}_j^z , \tag{2b}$$

$$H_{XXZ}\equiv-\hbar\sum_{j=1}^{N}[J(\hat{s}_j^{+}\hat{s}_{j+1}^{-}+\hat{s}_j^{-}\hat{s}_{j+1}^{+})+2J_z\hat{s}_j^z\hat{s}_{j+1}^z] . \tag{2c}$$

Here $\hbar\omega_0$ is the excitation energy of a molecule corrected by static dipolar interactions, $\hat{s}_j^z$ gives the population difference at the jth molecule, and a cyclic boundary condition is imposed, i.e., $\hat{s}_{N+1}^{\pm}=\hat{s}_1^{\pm}$ and $\hat{s}_{N+1}^z=\hat{s}_1^z$. Note that $\hat{s}_j^{\pm}$ and $\hat{s}_j^z$ satisfy the well-known commutation relations for spin operators:

$$[\hat{s}_i^{+},\hat{s}_j^{-}]=2\delta_{ij}\hat{s}_j^z,\ [\hat{s}_i^z,\hat{s}_j^{\pm}]=\pm\delta_{ij}\hat{s}_j^{\pm} . \tag{3}$$

Here we have kept in H_{XXZ} only the nearest-neighbor coupling, i.e.,

$$2\hbar J=-\frac{d^2}{4\pi\epsilon_0a^3}\left[1-\frac{3(\boldsymbol{\varepsilon}\cdot\mathbf{a})^2}{a^2}\right] , \tag{4a}$$

0163-1829/93/48(4)/2773(4)/$06.00

$$2\hbar J_z = -\frac{|\boldsymbol{\mu}_e|^2}{4\pi\epsilon_0 a^3}\left[1-\frac{3(\boldsymbol{\varepsilon}'\cdot\mathbf{a})^2}{a^2}\right] , \tag{4b}$$

where the vector $\mathbf{a}$ denotes the relative position between the nearest-neighbor atoms in a chain, $a \equiv |\mathbf{a}|$, and $\boldsymbol{\varepsilon}$ is the unit polarization vector of the atomic transition dipole moment and $\boldsymbol{\varepsilon}'$ is that of the static dipole moment $\boldsymbol{\mu}_e$ induced in the electronic excited state. We assume for simplicity no static dipole moment at the electronic ground state.

The superradiant emission is characterized by the pulse profile $I(t)$ and the time-resolved emission spectrum $I(\omega,t;\Delta t)$. The superradiant pulse profile $I(t)$ is expressed in terms of the expectation value of the electronic energy $\langle H_0\rangle_t \equiv \mathrm{Tr}[H_0\rho(t)]$ as

$$I(t) \equiv -(d/dt)\mathrm{Tr}[H_0\rho(t)] = \Gamma\omega_0 \mathrm{Tr}[\hat{S}^+\hat{S}^-\rho(t)] . \tag{5}$$

We define the time-resolved emission spectrum as follows:[6]

$$I(\omega,t;\Delta t) \equiv \frac{\Gamma\omega_0}{\Delta t}\int_{-\Delta t/2}^{\Delta t/2} d\tau_1 \times \int_{-\Delta t/2}^{\Delta t/2} d\tau_2 \langle \hat{S}^+(t+\tau_1)\hat{S}^-(t+\tau_2)\rangle \times e^{-i\omega(\tau_1-\tau_2)} . \tag{6}$$

This expression describes the measurement of the emitted light by opening the slit between $t-\Delta t/2$ and $t+\Delta t/2$ and taking the Fourier transform of the signal in this time interval. We can evaluate Eqs. (5) and (6) by choosing appropriate basis vectors $\{|\mathbf{v}\rangle\}$. We used the simultaneous eigenvectors of H_I[$J=0$ in Eq. (2c)] and translational operator for practical calculations. Then the pulse profile $I(t)$ is rewritten as

$$I(t) = \Gamma\omega_0 \sum_{\mathbf{v},\mathbf{v}',\mathbf{v}''} \langle \mathbf{v}'|\rho(t)|\mathbf{v}''\rangle\langle \mathbf{v}''|\hat{S}^+|\mathbf{v}\rangle\langle \mathbf{v}|\hat{S}^-|\mathbf{v}'\rangle . \tag{7}$$

To evaluate the correlation function $\langle \hat{S}^+(t)\hat{S}^-(t+\tau)\rangle$, we use the quantum regression theorem.[11] We introduce the Liouville operator $\hat{L}(t)$ as $\rho(t+\tau) \equiv \hat{L}(\tau)\rho(t)$. Then

$$\begin{aligned}\langle \hat{S}^-(t+\tau)\rangle &= \mathrm{Tr}[\hat{S}^-\hat{L}(\tau)\rho(t)]\\ &= \sum_{\mathbf{v}\mathbf{v}'} \langle \mathbf{v}|\hat{S}^-|\mathbf{v}'\rangle\langle \mathbf{v}'|\hat{L}(\tau)\rho(t)|\mathbf{v}\rangle\\ &= \sum_{\mathbf{v}\mathbf{v}'}\sum_{\mathbf{v}_1\mathbf{v}_2} \langle \mathbf{v}|\hat{S}^-|\mathbf{v}'\rangle O^{\mathbf{v}\mathbf{v}'}_{\mathbf{v}_1\mathbf{v}_2}(\tau)\langle \mathbf{v}_1|\rho(t)|\mathbf{v}_2\rangle\\ &= \sum_{\mathbf{v}_1\mathbf{v}_2} Q_{\mathbf{v}_1\mathbf{v}_2}(\tau)\mathrm{Tr}[|\mathbf{v}_2\rangle\langle \mathbf{v}_1|\rho(t)] ,\end{aligned} \tag{8a}$$

where

$$Q_{\mathbf{v}_1,\mathbf{v}_2}(\tau) \equiv \sum_{\mathbf{v}\mathbf{v}'} \langle \mathbf{v}|\hat{S}^-|\mathbf{v}'\rangle O^{\mathbf{v}\mathbf{v}'}_{\mathbf{v}_1\mathbf{v}_2}(\tau) . \tag{8b}$$

Then the correlation function is expressed by using the quantum regression theorem as

$$\begin{aligned}\langle \hat{S}^+(t)\hat{S}^-(t+\tau)\rangle &= \sum_{\mathbf{v}_1\mathbf{v}_2} Q_{\mathbf{v}_1\mathbf{v}_2}(\tau)\mathrm{Tr}[\hat{S}^+|\mathbf{v}_2\rangle\langle \mathbf{v}_1|\rho(t)]\\ &= \sum_{\mathbf{v}_1\mathbf{v}_2}\sum_{\mathbf{v}''} Q_{\mathbf{v}_1\mathbf{v}_2}(\tau)\langle \mathbf{v}''|\hat{S}^+|\mathbf{v}_2\rangle\langle \mathbf{v}_1|\rho(t)|\mathbf{v}''\rangle .\end{aligned} \tag{9}$$

The finite matrix elements of the density operator $\langle \mathbf{v}_1|\rho(t)|\mathbf{v}''\rangle$ are chosen as a vertical vector and the master equation (1) is numerically solved as linear coupled equations. The matrix element of the Liouville operator $O^{\mathbf{v}\mathbf{v}'}_{\mathbf{v}_1\mathbf{v}_2}$ is similarly evaluated with the initial condition $\langle \mathbf{v}_1|\rho|\mathbf{v}_2\rangle = 1$ at $\tau=0$.

First we will discuss several limiting cases.

(i) $J=J_z=0$. This is the celebrated Dicke's superradiance. The master equation becomes

$$\frac{d\rho}{dt} = -\hat{\Gamma}\rho - i[\Omega_0,\rho] , \tag{10}$$

where $\hbar\Omega_0 = H_0$. Equation (10) has been investigated in many articles.[1-3]

(ii) $J_z=0$. The Hamiltonian H_{XXZ} reduces to the $XX0$ Hamiltonian. This case was already investigated in Refs. 5 and 6, where a Jordan-Wigner transformation was used to diagonalize the Hamiltonian and chirping and slow emission tails were demonstrated in the time-resolved emission spectrum and the superradiant pulse profile.

(iii) $J=J_z$. This corresponds to the Heisenberg limit of the XXZ model: $H_{XXZ}\rightarrow H_H$. Because of its $sl(2)$ symmetry, namely,

$$[H_H,\hat{S}^z] = [H_H,\hat{S}^\pm] = 0 , \tag{11}$$

H_H commutes with both H_0 and $\hat{\Gamma}$:

$$[H_H,H_0] = 0 , \tag{12}$$

$$\hat{\Gamma}[H_H,\rho] = [H_H,\hat{\Gamma}\rho] = 0 . \tag{13}$$

Therefore, when we define

$$\tilde{\rho}(t) \equiv e^{(i/\hbar)H_H t}\rho(t)e^{-(i/\hbar)H_H t} , \tag{14}$$

$\tilde{\rho}$ satisfies Dicke's superradiance master equation Eq. (10):

$$\frac{d\tilde{\rho}}{dt} = -\hat{\Gamma}\tilde{\rho} - i[\Omega_0,\tilde{\rho}] . \tag{15}$$

Furthermore, due to the symmetry Eq. (11), the expectation value of an arbitrary operator composed of $\hat{S}^+,\hat{S}^-$ and $\hat{S}^z,\hat{F}(\hat{S}^+,\hat{S}^-,\hat{S}^z)$, can be evaluated as

$$\begin{aligned}\langle \hat{F}(\hat{S}^+,\hat{S}^-,\hat{S}^z)\rangle_t &\equiv \mathrm{Tr}[\hat{F}(\hat{S}^+,\hat{S}^-,\hat{S}^z)\rho(t)]\\ &= \mathrm{Tr}[\hat{F}(\hat{S}^+,\hat{S}^-,\hat{S}^z)e^{-(i/\hbar)H_H t}\tilde{\rho}(t)e^{(i/\hbar)H_H t}]\\ &= \mathrm{Tr}[\hat{F}(\hat{S}^+,\hat{S}^-,\hat{S}^z)\tilde{\rho}(t)] .\end{aligned} \tag{16}$$

Thus we can conclude that the emission profile in the Heisenberg limit is exactly the same as in the Dicke's superradiance since it can be obtained by $\langle \hat{S}^-\rangle_t$ and $\langle \hat{S}^+\hat{S}^-\rangle_t$.

(iv) $J=0$. The Hamiltonian becomes that of the Ising model:

$$H_I = -2\hbar J_z \sum_{j=1}^{N} \hat{s}_j^z \hat{s}_{j+1}^z \ . \tag{17}$$

The eigenenergy of $H_{ex}=H_0+H_I$ can be described as a simple product of local spin vectors such as

$$|\uparrow\rangle_1 \otimes |\downarrow\rangle_2 \otimes \cdots \otimes |\downarrow\rangle_N \ , \tag{18}$$

where $|\uparrow\rangle_j(|\downarrow\rangle_j)$ denotes the up-spin (down-spin) state at the jth site.

The eigenstate is described by the number difference between the up-spin (excited) states and the down-spin (ground) states $(N_+ - N_-)\equiv 2m$, and the number q of the pairs $(|\downarrow\rangle_j \otimes |\uparrow\rangle_{j+1})$ or that of pairs $(|\uparrow\rangle_j \otimes |\downarrow\rangle_{j+1})$, which are equal to each other under the cyclic boundary condition. Then the eigenenergy is expressed by

$$\begin{aligned}(H_0+H_I)|m,q\rangle_I &= E_I(m,q)|m,q\rangle_I \\ &= \hbar\left[m\omega_0 + 2qJ_z - \frac{N}{2}J_z \right]|m,q\rangle_I \ .\end{aligned} \tag{19}$$

For every spontaneous emission of one photon from this system, the quantum number m decreases by one and the change in q can assume one of the three values $\Delta q = 0$ and $\Delta q = \pm 1$. Therefore we have three emission lines at

$$\begin{aligned}\omega &= \{E_I(m,q)-E_I(m-1,q')\}/\hbar \\ &= \begin{cases} \omega_0 - 2J_z & (\text{ for } \Delta q = q - q' = -1) \\ \omega_0 & (\text{ for } \Delta q = 0) \\ \omega_0 + 2J_z & (\text{ for } \Delta q = 1) \ . \end{cases}\end{aligned} \tag{20}$$

When the system is in the strongly population-inverted state, the emission channel of $\Delta q = -1$ is dominant, while in the weakly excited state that of $\Delta q = 1$ is dominant. Thus we expect that the emission line of the superradiant pulse is first at the frequency of $\omega_0 - 2J_z$, then lines at ω_0 and $\omega_0 + 2J_z$ appear successively, and finally the line at $\omega_0 + 2J_z$ remains.

The eigenenergies with the same quantum number m differ from each other by a multiple of $2\hbar J_z$, so that the interference between the macroscopically induced polarization will have the period $1/(2J_z)$. We expect that such oscillation may have some effect on the emission profile.

We will show numerical results for the system of six molecules for general cases as well as the discussed limiting cases. We will vary the parameters J and J_z under a constraint $(J^2+J_z^2)^{1/2}=2.0$. The energy is measured in units of $(J^2+J_z^2)^{1/2}/2=1$ (hereafter $\hbar=1$).

The superradiant pulse profile $I(t)$ is drawn in Fig. 1 for several relative values of J_z to J. The Heisenberg model exhibits the same shortest pulse profile as Dicke's superradiance from noninteracting atoms (molecules), as Fig. 1(a) shows. This is because the Heisenberg and Dicke models give the same correlation function, i.e., the same superradiant response as shown by Eqs. (11)–(16). The oscillatory structure is superposed on the superradiant pulse profile of the Ising model, as Fig. 1(d) shows. This comes from the interference among the transitions with the three frequencies $\omega_0 - 2J_z$, ω_0, and $\omega_0 + 2J_z$. Other cases such as $XX0$ and XXZ models have also slow components, as Figs. 1(b) and 1(c) show.

The time-resolved emission spectra of the superradiant emission are calculated and shown in Fig. 2. The spontaneous emission rate Γ of a single molecule is chosen to

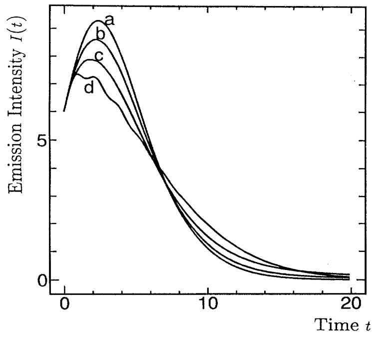

FIG. 1. Superradiant pulse profile $I(t)$. (a) Heisenberg model ($J=J_z=1.41$), (b) $XX0$ model ($J=2.00, J_z=0$), (c) XXZ model ($J=1.41, J_z=-1.41$), and (d) Ising model ($J=0, J_z=2.00$).

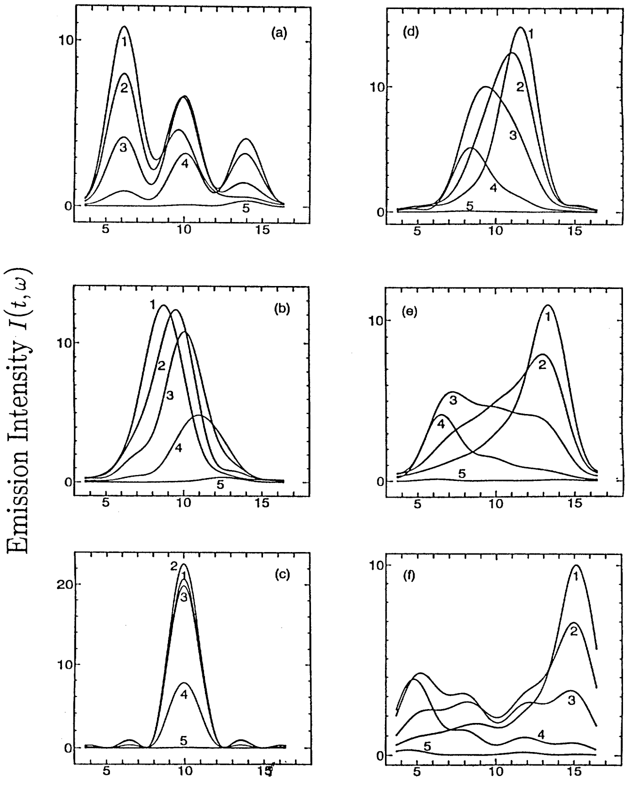

FIG. 2. Time-resolved emission spectrum. (a) Ising model ($J=0, J_z=2.00$), (b) XXZ model ($J=0.765, J_z=1.85$), (c) Heisenberg model ($J=J_z=1.41$), (d) XXZ model ($J=1.85$, $J_z=0.765$), (e) $XX0$ model ($J=2.00, J_z=0$), and (f) XXZ model ($J=1.41, J_z=-1.41$). The numbers in the figures mean the time at which the spectrum is measured with the slit time width $\Delta t=2.56$, i.e., (1) $t=1.28$, (2) 2.30, (3) 4.00, (4) 7.50, and (5) 18.0.

be 0.1 with the energy unit $(J^2+J_z^2)^{1/2}/2=1.0$. The time-resolved emission spectrum of the Ising model with $J=0$ and $J_z=2.0$ consists of three peaks at ω_0-2J_z, ω_0, and ω_0+2J_z. At the initial stage, the emission at the lowest component $\omega=\omega_0-2J_z=6.0$ is the strongest; then three peaks come to have the same order of magnitude and finally the highest component becomes strongest. This frequency shifting can be explained as follows: All spins are in the up-spin state at the beginning so that a deexcitation induces two pairs of up- and down-spin states and increases the interacting energy by $2J_z$. This emission has a transition energy ω_0-2J_z. Conversely, the number of up- and down-spin pairs decreases by annihilation of excitations at the final stage. This gives the emission peak at ω_0+2J_z. For the case between the Heisenberg and Ising models, i.e., $J=0.765$ and $J_z=1.85$, the redshift at the initial stage and the blueshift at the final stage become weaker than the case of the Ising model as shown in Fig. 2(b). For the Heisenberg model, the emission peak is always at $\omega=\omega_0$, as discussed already and shown in Fig. 2(c). When the dipolar interactions $J=1.85$ and $J_z=0.765$ are chosen to be just halfway between the Heisenberg and *XX*0 models, the sign of shifts is reversed, i.e., the blueshift at the initial stage and the redshift at the final stage, as Fig. 2(d) shows. For the *XX*0 model, $J=2.0$ and $J_z=0$, the magnitude of the blueshifts and redshifts increases, as Fig. 2(e) shows. Finally, this increases furthermore when we choose $J=1.41$ and $J_z=-1.41$. The sign change of J_z is realized when the static dipole moments are induced in the direction perpendicular to the chain axis as can be read from Eq. (4b). The sign change of J is realized, e.g., in *H* aggregates in which the transition dipole moment is also perpendicular to the chain axis [see Eq. (4a)]. The sign of frequency shift is changed in this case, but we did not discuss it in this paper.

In conclusion, we have described the superradiance of Frenkel excitons interacting via static dipole moments in terms of the spin-half *XXZ* model. We have found first that this system of Frenkel excitons can be described by the spin-half Heisenberg model when the transition dipole moment d and the induced static dipole moment $|\boldsymbol{\mu}_e|$ are equal to each other and that this system shows the same superradiance as Dicke's one from noninteracting two-level system. Second the system described by the Ising spin model, in which $|\boldsymbol{\mu}_e|$ is much larger than d, shows the superradiant pulse profile oscillating in time and the chirping, i.e., the redshifts and blueshifts, respectively, at the initial and final stages of the emission pulse, which is opposite in sign to the case of the *XX*0 model. Third, we have obtained characteristic features for the general cases with arbitrary ratio of J_z/J. When the static dipole moment induced in the excited state is perpendicular to the chain axis, the redshifts and blueshifts, respectively, at the initial and final stages, are further enhanced in comparison to the *XX*0 model with $J_z=0$ but the same value $(J^2+J_z^2)^{1/2}=2.0$. We have many kinds of *J* aggregates of dyes and charge-transfer excitons to which the present model is applicable. The charge-transfer excitons, e.g., in anthracene PMDA have large static dipole moments in the chain direction so that $J_z/J>1$, and both J_z and J are positive. However, the excitons in *J* aggregates of dyes have the directions and magnitudes of transition and static dipole moments depending upon the kinds of dyes. The problem of these systems, however, is that these organic materials are rather weak against such strong pumping as the population inversion is realized. In this respect, the excitons bound to imputities regularly arrayed in semiconductors are more likely to show the results proposed in the present paper.[6]

We have assumed the complete population inversion for the initial state. The superradiance from the arbitrary initial state is one of the future problems. The extension to a two- or three-dimensional system or to the Wannier excitons is also another problem for future work.

This work was supported by Grant-in-Aid for Scientific Research on Priority area, "Electron Wave Interference Effects in Mesoscopic Structures" and "Electronic Properties of Mesoscopic Particles" from the Ministry of Education, Science and Culture of Japan. It was also supported by the cooperative research between Japan and USA sponsored by NEDO's International Joint Research Program and Japan Promotion of Sciences.

---

[1] R. H. Dicke, Phys. Rev. **93**, 99 (1954).

[2] N. Skribanowitz, I. P. Herman, J. C. MacGillivray, and M. S. Feld, Phys. Rev. Lett. **30**, 309 (1973).

[3] Q. H. F. Vrehen, H. M. J. Hikspoors, and H. M. Gibbs, Phys. Rev. Lett. **42**, 224 (1979).

[4] For example, R. S. Knox, *Theory of Excitons* (Academic, New York, 1963).

[5] E. Hanamura, T. Tokihiro, and Y. Manabe, in *Science and Technology of Mesoscopic Structures,* edited by S. Namba, C. Hamagchi, and T. Ando (Springer-Verlag, Heidelberg, 1992), p. 434.

[6] T. Tokihiro, Y. Manabe, and E. Hanamura, Phys. Rev. B **47**, 2019 (1993).

[7] S. de Boen, K. J. Vink, and D. A. Wiersma, Chem. Phys. Lett. **137**, 99 (1987).

[8] H. Fidder, J. Knoester, and D. A. Wiersma, Chem. Phys. Lett. **171**, 529 (1990); J. Chem. Phys. **95**, 7880 (1991), and references cited in these papers.

[9] R. H. Lehmberg, Phys. Rev. A **2**, 883 (1970); **2**, 889 (1970).

[10] M. Gross and S. Haroche, Phys. Rep. **93**, 301 (1982).

[11] M. Lax, Phys. Rev. **172**, 350 (1968).