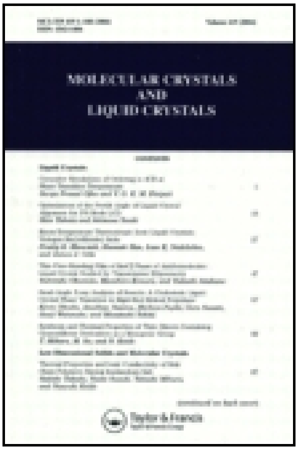

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NONLOCAL OPTICAL RESPONSE OF MESOSCOPIC AGGREGATES OF POLYMERS

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Linear absorption of nanometer scale aggregates of polymers are studied using the nonlocal response theory. Besides the main peak around the exciton levels, additional peaks appears due to the interaction with radiation field, and their size dependence is discussed.

Keywords: nonlocal response theory; conjugated polymers; nanometer scale

INTRODUCTION

In the study of spectroscopy of nano-meter scale structures, special care is needed bacause of the following factors.

1)The existance of surface: in a nano-meter scale structure, the surface effect would be more important compared to the bulk.

2)Coherence: the small (nano-meter scale) system keeps coherence of wave functions through it.

3)Confinement: the quantum states take discrete levels.

Moreover, in molecular aggregates, the interaction between matter and radiation field is very large. So we caluclated the linear absorption spectra of molecular aggregates of nano-meter scale using the nonlocal response theory [1],[2],[3], which takes into account the nonlocality of the response function.

In the following sections, we show caluculations of linear absorption spectra of slab aggregates and of cylindrical aggregates, and the usefulness of the nonlocal response theory is demonstrated.

NONLOCAL RESPONSE THEORY

In a mesoscopic system the coherence of the wave functions is spread over the system. In this case, the conventional expression for the electric polarization,

$$\boldsymbol{P}(\boldsymbol{r},\omega) = \chi(\omega)\boldsymbol{E}(\boldsymbol{r},\omega). \tag{1}$$

is not correct. The polarization is affected by electric fields from all parts of the system so that $\boldsymbol{P}(\boldsymbol{r},\omega)$ is expressed nonlocally as

$$\boldsymbol{P}(\boldsymbol{r},\omega) = \int \chi^{(1)}(\boldsymbol{r},\boldsymbol{r}',\omega)\boldsymbol{E}(\boldsymbol{r}',\omega)d\boldsymbol{r}'. \tag{2}$$

The polalizability χ is expressed as

$$\chi^{(1)}(\boldsymbol{r},\boldsymbol{r}',\omega) = \sum_{\lambda}[\frac{<0|\boldsymbol{p}(\boldsymbol{r})|\lambda><0|\boldsymbol{p}(\boldsymbol{r}')|\lambda>}{E_\lambda - \hbar\omega - i\gamma} + \frac{<0|\boldsymbol{p}(\boldsymbol{r}')|\lambda><0|\boldsymbol{p}(\boldsymbol{r})|\lambda>}{E_\lambda + \hbar\omega + i\gamma}] \tag{3}$$

where λ denotes a quantum state of the system.

On the other hand, the electric field $\boldsymbol{E}(\boldsymbol{r},\omega)$ is determined by polarization $\boldsymbol{P}(\boldsymbol{r},\omega)$ through the Maxwell equations. So $\boldsymbol{E}$ and $\boldsymbol{P}$ have to be solved self-consistently. These equations (the Maxwell equations and eq.(2)) can be rewritten as linear simultaneous equations, which can be easily solved[1],[2],[3].

Assuming an incident plane wave E_i , we can calculate reflecting and transmitting waves in the case of a slab, and scattered waves in the case of a cylinder, by using the Maxwell boundary condition. The linear absorption is expressed as the difference between the energies of electromagnetic fields flowing into the system and going out of the system.

RESULTS

By using the nonlocal theory described above, we calculated the linear absorption of slabs and cylinders of various sizes (slab thickness L_z or cylinder diameter D). Each system consists of a regular array of identical molecules.

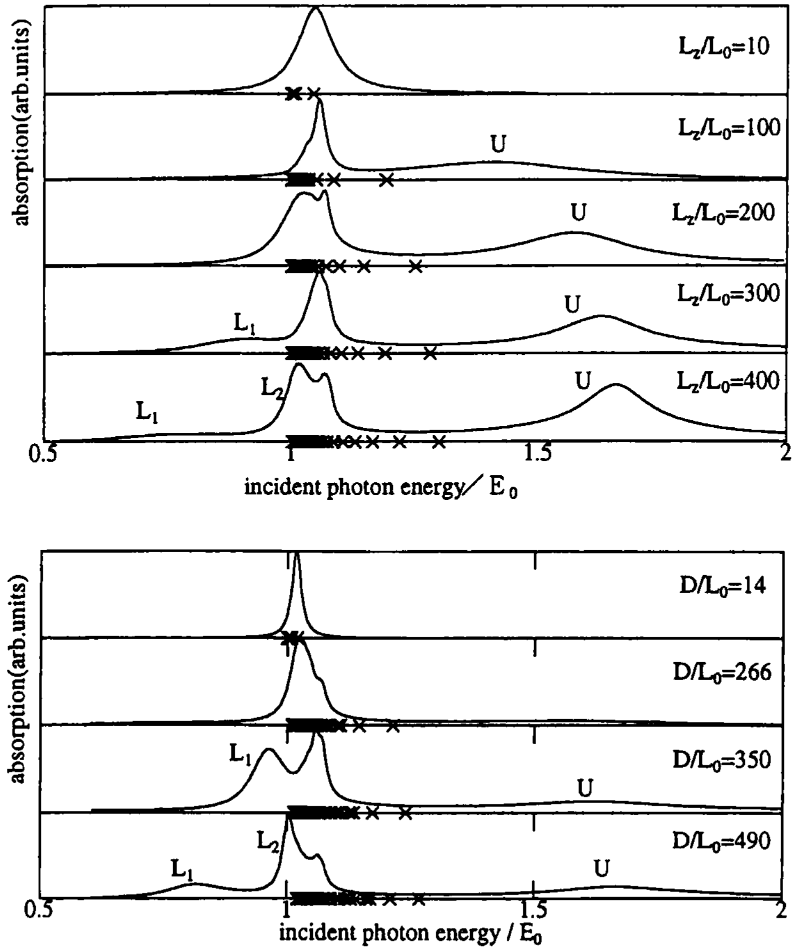

Figure 1: linear absorption spectra of the slab(above) and the cylinder(below). × denotes the exciton energies

We use the following parameters. The distance L_0 between adjacent molecules is $4\AA$. The molecule has $400\AA$ length, electronic transition energy $E_0 = 2eV$ and transition dipole moment $\mu = 10\AA$ parallel to its long axis. The interaction between molecules is expressed by the extended dipole model[4][6], and the Frenkel type exciton is considered. The damping constant γ introduced in eq.(3) is the non-radiative decay rate of each exciton state. Other than this, radiative damping appears after solving the Maxwell equations and eq.(2). These damping mechanisms determine the absorption spectra calculated in the present paper. In the following $\gamma = E_0 \times 10^{-2}$ is assumed except in Fig.3 where the non-radiative decay rate γ is very small($E_0 \times 10^{-10}$) and the radiative damping is dominant.

For simplicity, the incident field is assumed to be parallel to the dipole. So the field is modulated only in the direction perpendicular to the molecular long axis.

Figure 1 shows linear absorption of slab aggregates and cylindrical aggregates for various sizes.

The peak around E_0 is due to absorption to exciton states. At the low energy side, we see other peaks (L_1, L_2) with strong size dependence. The polalization of the system at L_1 has one node inside the slab or the cylinder, corresponding to the wavefunction of the exciton of the second highest energy.

The size dependence of the peak energy is compared with the bulk polariton energy in Fig.2. For each system size, the energy of the bulk polariton with the wave length which equals to the system size and the energy of the bulk polariton with the wave length half of which equals to the system size are plotted in addition to the energies of peak L_1, L_2. The L_1 and L_2 peak positions coincide with the energy of the lower branch of the bulk polariton with the wave length half of which equals to the system size, the energy of the lower branch of the bulk polariton with the wave length which equals to the system size, respectively.

There is another peak (U) at the high energy side whose polarization has no node, corresponding to the wave function of the exciton with highest energy. The size dependence of this peak position does not reflect that of the bulk polariton very much (Fig.2).

Figure 3 shows radiative line width of each peak where the non-radiative decay rate is set small ($\gamma = E_0 \times 10^{-10}$) to reveal the radiative widths. When the system size is less than about 100, the width of the peak U increases linearly with the size, whereas other peaks have little width. For larger systems it becomes decreasing and other peaks have comparable widths.

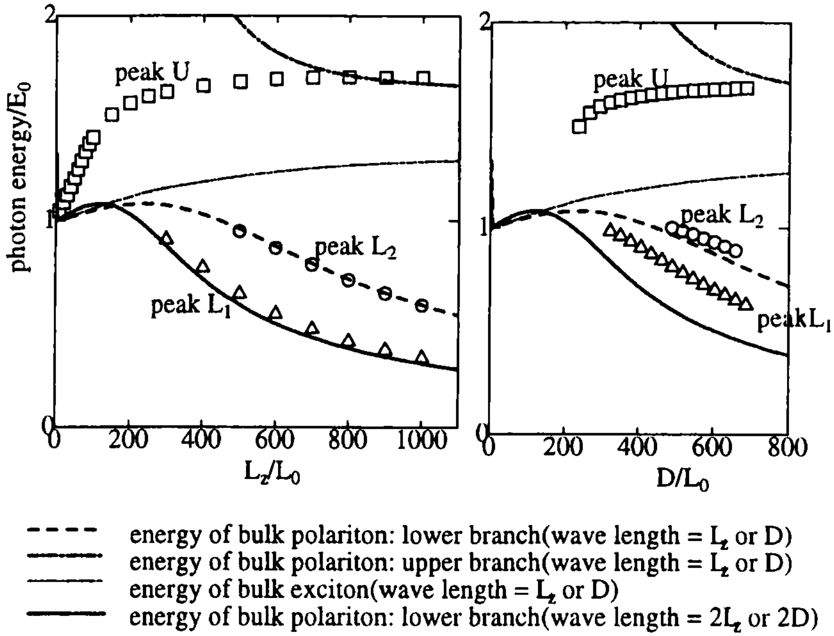

Figure 2: energies of peaks and bulk polariton as a function of system size

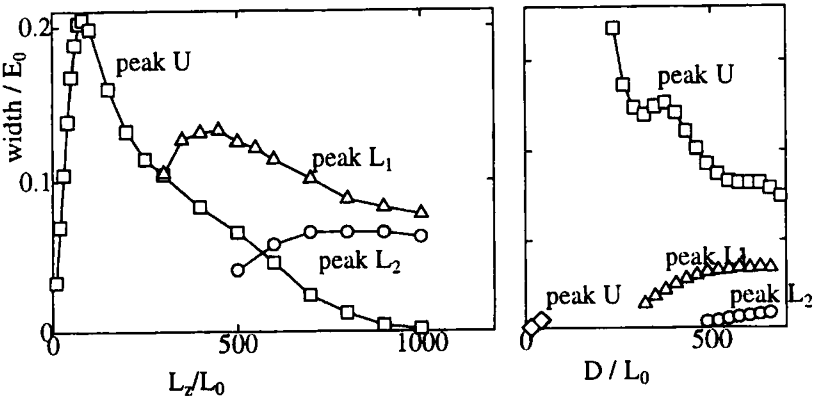

Figure 3: Size dependence of peak widths (half width at half maximum)

DISCUSSION

To understand the nature of the peaks L_1, L_2 and U we refer the work of Fuchs el al. [5] where the optical modes of vibration in slabs of ionic crystal is studied. They showed the existance of decaying modes which carry energy out of the slab. These modes are called virtual modes in the radiative region and shown to be related to the absorption. The absorption peaks calculated in present paper corresponds to these virtual modes.

The large width of U shows its enhanced spontaneous emission, which arises from the strong coupling with fields. In this mode, interaction with outside fields through the surface seems crucial. This makes the energy of U much different from that of the bulk polariton.

On the other hand, the energies of L_1, L_2 reflect bulk polariton energy, as mentioned above. This implies that the modes interact with the field inside the system and the existance of the surface is not very important for these states.

The existance of the additional peaks U, L_1, L_2 and their size dependence are obtained in systems smaller than the wave length of light. In these systems the polarization and fields are varying in smaller length scales than the wavelength of the incident field, and the results cannot be elucidated by neither a long-wave approximation nor a local response theory.

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