Finite-size effects in the exciton-phonon coupled system

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The size dependence of the optical spectra of the exciton-phonon coupled system is studied theoretically. As the sample size N increases, the optical spectrum generally crosses over from Gaussian to Lorentzian with motional narrowing due to the increased itineracy of the exciton. It is found that this crossover depends strongly on the ratios W/D and $W/(\hbar\omega_D)$ (W is the exciton bandwidth, D the site energy fluctuation, and ω_D the Debye frequency). Even nonmonotonic behavior is found in the numerical study.

The optical spectra of the exciton-phonon system are a powerful means to study its detailed dynamics.[1] In the strong coupling limit, the spectrum shows a Gaussian line shape. In weak coupling, on the other hand, it becomes typically a Lorentzian, characterizing the motional narrowing. These two cases are roughly distinguished by the relative magnitude of the site energy fluctuation D due to the phonon and the exciton bandwidth W. We use units where $\hbar=1$ and the lattice constant $a=1$. Assuming that the Debye frequency ω_D is much smaller than W, the correlation time τ_c of the site energy fluctuation is given by $1/\tau_c \sim W$. If one considers the relaxation function of the dipole moment as a function of a real time t, it decays with some time scale τ_R which gives the width of the line shape Γ as $\Gamma \sim 1/\tau_R$. When $\tau_c \gg \tau_R$, the site energy fluctuation can be regarded as static and the spectrum becomes a Gaussian with $\Gamma \sim D$. This happens when $D \gg W$. On the other hand, if $\tau_c \ll \tau_R$ motional narrowing occurs and the width Γ is estimated as $\Gamma \sim D^2\tau_c \sim D^2/W$. This corresponds to the case $D \ll W$. The crossover between these two can be observed in principle by changing the ratio D/W. Experimentally, however, abrupt change of the emission spectra was observed in the mixed crystal $AgBr_{1-x}Cl_x$ on changing the concentration x.[2] This has been interpreted as a discontinuous change between ''free'' and ''self-trapped'' excitons coupled with the phonon field. Another possible way of observing this crossover is to change the size of the sample N; this has been recently pursued experimentally. Especially in one-dimensional materials, because of the advantage that the system size along the one-dimensional axis can be controlled in some cases, many experimental studies have been done for polyenes,[3] polydiacetylene,[4] molecular aggregates,[5] and silicon oligomers.[6] The interest in these studies is mainly focused on the ordering and positions of the energy levels. Recently Kishida *et al.*[7] have studied in detail the line shapes of the absorption spectra in silicon oligomers on changing the chain length under the same experimental conditions. As the chain length increases, a *continuous* change of the spectral shape from Gaussian has been observed.

Inspired by these experimental works, in this paper we study theoretically finite-size effects on the optical spectra of excitons. Lu and Mukamel[8] addressed this problem, and studied numerically the optical spectra of a finite-size exciton-phonon coupled system by using dynamical coherent potential approximation (CPA). They calculated with several sets of parameters, but the global feature of crossovers was not revealed. Extending the generating function method devised by Toyozawa,[1] we propose a much simpler analytical theory and find that the behavior of the crossover is classified into three types depending on the two dimensionless ratios W/D and W/ω_D, which are assumed to be much larger than unity in this paper.

We start with the Hamiltonian for the Frenkel exciton coupled with the phonon field:

$$H = H_{\rm ex} + H_{\rm int} + H_{\rm ph} = \sum_k \varepsilon_k a_k^\dagger a_k + \sum_{i=1,N} \gamma Q_i a_i^\dagger a_i + H_{\rm ph} \tag{1}$$

where $a^\dagger$ (a) is the creation (annihilation) operator of the exciton, and ε_k is its energy dispersion. The Hamiltonian $H_{\rm ph}$ describes the phonon field Q_i, and the frequency ω_q of the phonon mode with the wave vector q is typically of the order of the Debye frequency ω_D. It should be noted that the wave vector k of the exciton is appropriately quantized due to the finite-size effect, while that of the phonon q is not because we consider the case where the finite-size molecule is embedded in the infinite reservoir of the phonon field.

Using the linear response theory, the absorption spectrum $I(\omega)$ is given by the Fourier transform of the relaxation function $F(t)$ of the dipole moment, which is given by Ref. 1:

$$F(t) = |M|^2 e^{-i\varepsilon_0 t} \langle\langle 0|\exp[iH_{\rm ex}t]\exp[-i(H_{\rm ex}+H_{\rm int})t]|0\rangle\rangle_{\rm ph} \tag{2}$$

where $|M|$ is the matrix element of the dipole moment, and $\langle\langle 0|\cdots|0\rangle\rangle_{\rm ph}$ means the expectation value with the exciton state of zero wave vector together with the average over the phonon thermal equilibrium. We employ the approximation that only the second order cumulant is kept, which is known to reproduce both the strong and weak coupling results:

$$F(t) \cong |P|^2 \exp[-i\varepsilon_0 t - C(t)] \tag{3}$$

where $C(t)$ is given by

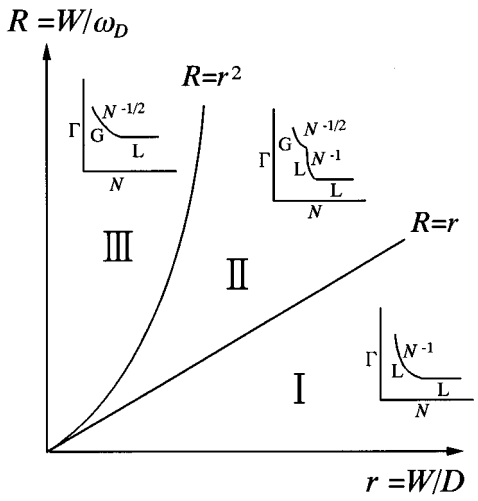

FIG. 1. Three types (I, II, and III) of the chain length (N) dependence of the line shape in the r-R plane ($r=W/D$, $R=W/\omega_D$ with W the exciton bandwidth, D the on-site energy fluctuation, and ω_D the Debye frequency). In the inset, the N dependence of the linewidth (Γ) is schematically depicted (G: Gaussian and L: Lorentzian).

$$C(t)=\int_0^t (t-\tau)\langle\langle 0|H_{\rm int}(\tau)H_{\rm int}(0)|0\rangle\rangle_{\rm ph}$$
$$=\frac{\gamma^2}{N}\sum_{m=0}^{N-1}\int_0^t (t-\tau)\langle Q(\tau)Q(0)\rangle\exp[i\Delta\varepsilon_m\tau]$$
$$\equiv\frac{1}{N}\sum_{m=0}^{N-1} f_m(t) \tag{4}$$

where k_m is the discretized wave vector of the exciton, and the exciton energy difference $\Delta\varepsilon_m=\varepsilon_{k_m}-\varepsilon_0$ is discretized as $\Delta\varepsilon_{m=1}\sim W/N^2$. We assume that the correlation function of the phonon is diagonal in the site representation, i.e., $\langle Q_i(t)Q_j(0)\rangle=\delta_{ij}\langle Q(t)Q(0)\rangle$. The function $\langle Q(t)Q(0)\rangle$ decays within the time scale of $1/\omega_D$. The site energy fluctuation due to the phonon is measured by $D^2=\langle\langle 0|[H_{\rm int}(0)]^2|0\rangle\rangle_{\rm ph}=\gamma^2\langle Q(0)^2\rangle$.

We are now interested in the N dependence of the function $C(t)$. In the limit of $N\to\infty$ the sum over k_m becomes the integral, and we assume it represents the weak coupling Lorentzian line shape in the infinite system, i.e.,

$$C_\infty(t)\cong(-i\Delta_\infty+\Gamma_\infty)t \tag{5}$$

where Δ_∞ and Γ_∞ are the shift and width of the spectrum, and this equation is valid for $t\gg 1/W$. As noted above $\Gamma_\infty\sim D^2/W$ is independent of ω_D. Then the finite-size correction to $C(t)$ is given approximately as

$$C_N(t)\sim\frac{1}{N}f_0(t)+C_\infty(t). \tag{6}$$

Now the function $f_0(t)$ behaves as

$$f_0(t)\sim D^2t^2 \quad \text{for} \quad t\ll 1/\omega_D,$$
$$f_0(t)\sim D^2t/\omega_D \quad \text{for} \quad t\gg 1/\omega_D. \tag{7}$$

Then the function $C_N(t)$ behaves approximately as

$$C_N(t)\sim D^2t/W \quad \text{for} \quad t\ll N/W,$$
$$C_N(t)\sim D^2t^2/N \quad \text{for} \quad N/W\ll t\ll 1/\omega_D,$$
$$C_N(t)\sim D^2\left(\frac{1}{N\omega_D}+\frac{1}{W}\right)t \quad \text{for} \quad 1/\omega_D\ll t, \tag{8}$$

when the size N is smaller than the ratio W/ω_D. It is noted that the t^2 region is between the two t regions, and $C_N(t=N/W)\sim D^2N/W$ increases and $C_N(t=1/\omega_D)\sim D^2/(N\omega_D^2)$ decreases as N. When $N>W/\omega_D$, on the other hand, $C_N(t)$ is approximated as $C_\infty(t)$, and the spectrum is identical to that of the infinite system. The width of the spectrum is determined by the time τ_R at which $|C_N(t_R)|\sim 1$ and the line shape is determined by the t dependence of $C_N(t)$ around t_R. Now we define the two dimensionless ratios as

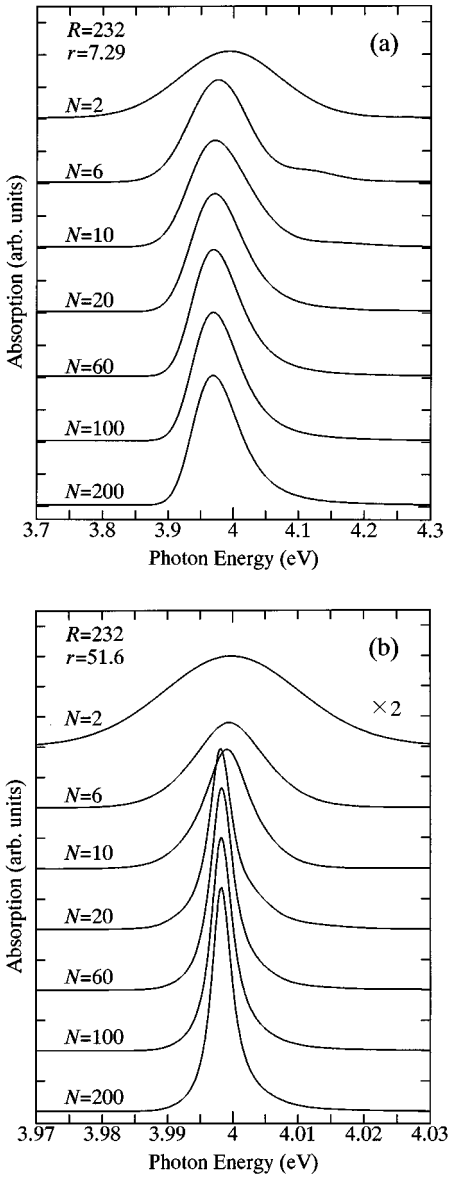

FIG. 2. Numerically calculated spectra in regions III (a) and II (b).

$R \equiv W/\omega_D$ and $r \equiv W/D$, both of which are assumed to be much larger than unity. Then there are three distinct behaviors of the finite-size effects depending upon R and r as shown in Fig. 1. In the region I in Fig. 1, i.e., $R<r$, $|C_N(1/\omega_D)| \sim R^2/(r^2 N) < 1$ and τ_R are always larger than $1/\omega_D$. Then the spectrum is always Lorentzian with $\Gamma \sim D^2[1/(N\omega_D)+1/W]$. In region II, i.e., $r<R<r^2$, $C_N(t=1/\omega_D) \sim D^2/(N\omega_D^2)$ becomes less than unity at $N=N_1=(R/r)^2$ before $C_N(t=N/W) \sim D^2 N/W$ becomes larger than unity at $N=N_2=r^2$. Then the spectrum is a Gaussian with the width $\Gamma \sim D/\sqrt{N}$ for $N<N_1=(R/r)^2$, while it becomes Lorentzian with $\Gamma \sim D^2(1/N\omega_D+1/W)$ for $N>N_1$. In the region III, on the other hand, $N_1>N_2$, and the spectrum crosses over from Gaussian to Lorentzian with $\Gamma \sim D^2/W$ for $N>N_2=r^2$. The line shape does not depend on the sample size once it becomes Lorentzian in this case, which is in contrast to region II.

We now present the numerical results of the optical spectrum for several parameters. Figure 2 shows the optical spectra calculated from Eqs. (3) and (4). The exciton band is assumed to be one dimensional and the periodic boundary condition is imposed. We take the phonon spectrum as that of the three-dimensional Debye model with the Debye cutoff ω_D. The parameters are set as follows: $\omega_D=100$ K, temperature $T=1000$ K, $W=2.0$ eV, and $r=51.6$ and 7.29. (This corresponds to $R=232$.) Figures 2(a) and 2(b) correspond to the parameters R and r in regions III and II, respectively, in the phase diagram Fig. 1.

In both figures a crossover of spectral shape as well as a narrowing happen with increase of the chain length. After the line shape becomes Lorentzian-like the width does not change so much in Fig. 2(a) compared with Fig. 2(b) as is expected from the discussion above. In Fig. 3 we plotted the half width at half maximum (HWHM) as a function of the chain length N for several values of r with fixed R. As r increases, the parameter point moves from region III to II. Roughly speaking the N dependence coincides with that expected in the discussion below Eq. (8). In the strong coupling region (small r), the HWHM shows only small and gradual ($N^{-1/2}$) decrease. On the other hand, in the weak coupling region (large r), the HWHM shows a steep decrease (N^{-1}) after an $N^{-1/2}$ decrease. Interestingly, however, the nonmonotonic N dependence is observed for $3.26<r<23.1$.

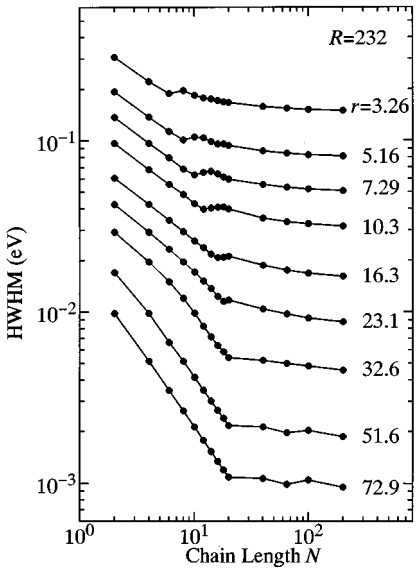

FIG. 3. Numerically calculated N dependence of values of the HWHM for several r with fixed $R=232$.

This is due to the breakdown of the approximation Eq. (6), which happens in one dimension where the contribution from the small k region to the integral in $C_\infty(t)$ is singular, and the divergence is cut off by ω_D. Then $C_\infty(t)$ depends on ω_D and cannot be approximated as $D^2 t/W$. In this case the finite-size correction can be different from Eq. (6), and nonmonotonic N dependence becomes possible as is seen in Fig. 3.

In summary, we have studied the finite-size effects on the optical spectra of an exciton-phonon coupled system. The crossover from strong coupling Gaussian to weak coupling Lorentzian spectra is found to be strongly dependent on the exciton bandwidth, Debye frequency, and site energy fluctuation due to the phonon. Also we found a possible nonmonotonic behavior as a function of the system size N.

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