Gain conditions for conducting polymer lasers

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Abstract

The condition of lasing threshold for solid-state conducting polymers is studied using a model Hamiltonian, which includes quasi-particles corresponding to both intrachain and interchain electronic excitations. We found that net gain can be achieved when the pump is so strong that intrachain and interchain species are mixed. A guide to overcome the difficulties coming from the photo-induced absorption due to the interchain excitations is proposed.

In addition to nonlinear optics and LED, the large electroluminescence quantum efficiency of conducting polymers suggests one further important area of applications: solid-state polymer-based lasers [1–3]. Besides the obvious advantages including the ease of processing, mechanical and optical strength and chemical flexibility, more importantly, the large band gap of conducting polymers (typically above 2 eV) implies the possibility of a new coherent light source in the green–blue regions, which is under strong demand. Net gain has been recently observed for polymer solution [1]. Radiative decay of the intrachain excitons are believed to be the origin of the gain. However, similar efforts for thin films encounter a serious difficulty: the gain is overwhelmed by the long-lived photo-induced absorption (PA) due to interchain excitations [2, 3], which are not present in the solution. Moreover, it is suggested that those interchain excitations are the predominant quasi-particles formed after photoexcitation [4].

In order to resolve this difficulty, we study theoretically the absorption spectrum of conducting polymers under optical pumping or electric current injection, and the condition under which the absorption turns to gain, i.e., negative absorption coefficient. In practice, lasing threshold is reached only after the gain overcomes the cavity loss, but we ignore such experimental details and are interested in only when the absorption becomes negative. The level of optical pumping or current injection, referred to generally as pumping later, is represented in terms of the total quasi-particle concentrations. It is found that as the concentration of the interchain excitations increase, the interchain distance will decrease, and consequently the coupling between the electronic states in different chains increase. Eventually, excitons and interchain excitations will be mixed and lose their identities. At the same time, the PA due to interchain excitations evolves into a gain, even if the interchain excitation is still the predominant species. This result suggests that polymers with side groups that mediate large interchain electronic coupling are more likely to be used for lasers. Note that the quasi-particle numbers are taken as adjustable

parameters. For a given pumping, their actual stationary values are determined by both the radiative and non-radiative lifetimes, which are somehow sample-dependent.

For simplicity, we consider only two chains. Relatively short chains with less than 20 monomers are implicitly assumed [4]. Exciton can be defined as the elementary excitation of only one chain alone in the absence of interchain coupling. Exciton number corresponds to the number of electron–hole pairs in the excitation. Spatial distribution and motions of the excitons, which are important for longer chains, are ignored here. When there is a weak coupling between the two chains, exciton remains approximately an excitation for the coupled system. Another kind of excitation, as previously mentioned, involves interchain charge transfer, and does not exist when there is only one chain. We name this interchain charge-transfer excitation "excimers". The terminology is due to the phenomenon that the interchain distance shrinks in the presence of such excitations, which is reminiscent of the excimers formed of usually smaller organic molecules [5]. We do not consider a first-principle approach here; instead, we take the quasi-particle picture that include excitons, excimers, and their essential interactions only. The optical absorption coefficient under pumping can be calculated explicitly using Kubo's formula [6].

Our Hamiltonian for the electronic part is

$$H_0 = \hbar\omega_e(Q)(e_1^\dagger e_1 + e_2^\dagger e_2) + \hbar\omega_x(a_1^\dagger a_1 + a_1^\dagger a_2)$$
$$+ \alpha(Q)(a_1^\dagger a_2 + a_2^\dagger a_1) + t(Q)$$
$$\times [(e_1^\dagger + e_2^\dagger)(a_1 + a_2) + \text{h.c.}]$$
$$+ \hbar\beta[(a_1^\dagger)^2(a_1)^2 + (a_2^\dagger)^2(a_2)^2]. \quad (1)$$

$a_{1(2)}^\dagger$ is the creation operator of one exciton in chain 1(2), while $e_{1(2)}^\dagger$ is the creation operator of one excimer with one electron transfered from chain 1(2) to chain 2(1). $a_{1,2}$ and $e_{1,2}$ satisfy the boson commutation relations [7]. $\hbar\omega_e$ and $\hbar\omega_x$ are the creation energies of one exciton and one excimer, respectively. α is the coupling constant for interchain hopping of the excitons. t is the coupling constant for interchain electron hopping that transfers excimers to excitons and vice versa. $\hbar\beta$ is the exciton self-interaction constant [7–9]. Q is the interchain distance. $\hbar\omega_x$ and $\hbar\beta$ do not depend on

Q, since they involve only one chain. There is no interchain excimer hopping terms, because such hopping requires two simultaneous electron transfers. In addition to the electronic Hamiltonian, there is a potential energy term $U = \frac{1}{2}K(Q - Q_0)^2$ due to the interchain elastic interaction. Q_0 is the interchain distance without any excitations. Q is determined by the level of pumping as follows. For given quasi-particle occupation numbers, the total energy E is equal to $U + \langle H_0 \rangle \simeq U(Q) + 2(\langle e_1^\dagger e_1 \rangle + \langle e_2^\dagger e_2 \rangle)\hbar\omega_e(Q) + \text{const}$. The actual Q is the one that minimizes $E(Q)$. "Const." means Q-independent terms. In order to study the absorption of the electromagnetic wave that propagates in the media, we consider an interaction Hamiltonian

$$H_1 = -(P^\dagger e^{-i\omega t} + P e^{i\omega t})\varepsilon, \quad (2)$$

and the total Hamiltonian is $H_0 + H_1$. P is the polarization of the coupled system, and can be written as [9]

$$P = \hbar g_e(e_1 + e_2) + \hbar g_x(a_1 + a_2).$$

ε and ω are the amplitude and frequency of the electromagnetic wave. $\hbar g_e$ and $\hbar g_x$ are the coupling constants to the electromagnetic field, and are proportional to the transition matrix element for the creation of an excimer and an exciton, respectively. Under pumping, the exciton–excimer system may be driven far away from the ground state, and the propagating wave may experience net gain. In order to calculate the absorption coefficient, we need to calculate the linear susceptibility, which is the linear response function for the polarization under the external electric field ε.

According to the Kubo's formula, the linear response function $\chi(t, t')$ is equal to the commutator

$$\chi(t, t') = i\langle [P(t), P^\dagger(t')] \rangle \theta(t - t').$$

Due to time translational invariance, χ is a function of $t - t'$ only and is written as $\chi(t)$ in the following. $\theta(t)$ is the step function. The time evolution of $P(t)$ is governed by H_0 only. Although simple, our model contains three basic physical properties: (1) net gain when only the exciton terms are retained, (2) PA due to excimer formation for weak pumping, and most importantly (3) gain due to excimer for stronger pumping. The nonlinear term $\hbar\beta [(a_1^\dagger)^2(a_1)^2 + (a_2^\dagger)^2(a_2)^2]$ is required in order to

obtain property (1). This can be easily understood. Consider excitons only. With the nonlinear term, for each chain the eigenstates of the Hamiltonian are still the eigenstates of the exciton occupation number $a^\dagger a$. However, the corresponding eigen energies grow superlinearly with respect to the exciton number. Therefore, photoabsorption (create one more exciton) and stimulated emission (destroy one existing exciton) will happen at different energies. Consequently, when the initial exciton number is large enough, the stimulated emission is not overwhelmed by the absorption even with certain broadening mechanisms. Explicit calculation confirms this point. We do not include a similar nonlinear term for the excimers, because no evidence of stimulated emission due to excimers were observed so far.

In order to obtain the susceptibility $\chi(t)$, we need the following 16 correlation functions:

$$\begin{pmatrix} \langle a_1(t)a_1^\dagger \rangle \\ \langle a_2(t)a_1^\dagger \rangle \\ \langle e_1(t)a_1^\dagger \rangle \\ \langle a_2(t)a_1^\dagger \rangle \end{pmatrix}, \quad \begin{pmatrix} \langle e_1(t)e_1^\dagger \rangle \\ \langle e_2(t)e_1^\dagger \rangle \\ \langle a_1(t)e_1^\dagger \rangle \\ \langle a_2(t)e_1^\dagger \rangle \end{pmatrix},$$

$$\begin{pmatrix} \langle a_1^\dagger a_1(t) \rangle \\ \langle a_1^\dagger a_2(t) \rangle \\ \langle a_1^\dagger e_1(t) \rangle \\ \langle a_1^\dagger e_2(t) \rangle \end{pmatrix}, \quad \begin{pmatrix} \langle e_1^\dagger e_1(t) \rangle \\ \langle e_1^\dagger e_2(t) \rangle \\ \langle e_1^\dagger a_1(t) \rangle \\ \langle e_1^\dagger a_2(t) \rangle \end{pmatrix}.$$

They are referred to as column vectors V_1, V_2, V_3 and V_4 later, respectively. Note that because of the symmetry between two polymer chains, the exchange of indices 1 and 2 gives the same correlation function. Due to the nonlinear term in H_0, this model cannot be solved exactly. We take the equation of motion approach for the correlation functions and make random-phase approximation (RPA) to close the equations, as outlined by the following example. The equation of motion for $V_{11} \equiv \langle a_1(t)a_1^\dagger \rangle$ is $i\hbar \dot{V}_{11} = \langle [a_1(t), H_0] a_1^\dagger \rangle = \hbar\omega_x V_{11} + \alpha V_{12} + t(V_{13} + V_{14}) + 2\hbar\beta \langle a_1^\dagger(t)a_1^2(t) a_1^\dagger \rangle$. Using RPA, we have

$$\langle a_1^\dagger(t)a_1^2(t)a_1^\dagger \rangle \simeq \langle a_1^\dagger(t)a_1(t) \rangle \langle a_1(t)a_1^\dagger \rangle < n_x V_{11}.$$

Hence $n_x \equiv \langle a_1^\dagger a_1 \rangle = \langle a_2^\dagger a_2 \rangle$ is the mean exciton number per chain due to pumping. Similarly, n_e is the mean occupation number of excimers. They are

assumed to stay constant and are taken as parameters in our model. RPA here corresponds to the assumption that our system, while being driven away from the ground state, is still a statistical mixture made of states that are approximately eigenstates of the exciton and excimer occupation number operators. Similarly, in the equation of motion for V_{31}, we get

$$\langle a_1^\dagger a_1^\dagger(t) a_1^2(t) \rangle = -\langle a_1^\dagger a_1(t) \rangle + \langle a_1^\dagger a_1(t) a_1^\dagger(t) a_1(t) \rangle$$

$$\simeq \langle a_1^\dagger a_1(t) \rangle > (-1 + n_x)$$

$$= V_{31}(-1 + n_x).$$

With RPA, the equations of motion for V_1–V_4 are linear and independent of each other. Explicitly, we have $i\hbar \dot{V}_n = M_n V_n$, for $n = 1, 2, 3, 4$. The 4×4 matrices are

$$M_1 = \begin{pmatrix} a & \alpha & t & t \\ \alpha & a & t & t \\ t & t & \hbar\omega_e & 0 \\ t & t & 0 & \hbar\omega_e \end{pmatrix},$$

$$M_2 = \begin{pmatrix} \hbar\omega_e & 0 & t & t \\ 0 & \hbar\omega_e & t & t \\ t & t & a & \alpha \\ t & t & \alpha & a \end{pmatrix},$$

$$M_3 = \begin{pmatrix} a' & \alpha & t & t \\ \alpha & a' & t & t \\ t & t & \hbar\omega_e & 0 \\ t & t & 0 & \hbar\omega_e \end{pmatrix},$$

$$M_4 = \begin{pmatrix} \hbar\omega_e & 0 & t & t \\ 0 & \hbar\omega_e & t & t \\ t & t & a' & \alpha \\ t & t & \alpha & a' \end{pmatrix}, \tag{3}$$

where $a \equiv \hbar\omega_x + 2\hbar\beta n_x$, and $a' \equiv \hbar\omega_x + 2\hbar\beta (-1 + n_x)$. The initial condition is determined by the equal-time correlation functions. We assume that the only non-zero ones are: $V_{11}(0) = \langle a_1 a_1^\dagger \rangle = n_x + 1$, $V_{21}(0) = \langle e_1 e_1^\dagger \rangle = n_e + 1$, $V_{31}(0) = \langle a_1^\dagger a_1 \rangle = n_x$, and $V_{41}(0) = \langle e_1^\dagger e_1 \rangle = n_e$. With the initial conditions, the 16 correlation functions can be solved analytically. After substituting into

the polarization P, we find the commutator of the form

$$\langle [P(t), P^\dagger(0)] \rangle = \sum_{i=1}^{4} A_i e^{-i\lambda_i t/\hbar}.$$

The susceptibility is

$$\chi(\omega) = i \int_{-\infty}^{0} \langle [P(t), P^\dagger(0)] \rangle e^{-i\omega t} dt$$

$$= \sum_{i=1}^{4} - A_i \frac{1}{\omega - \lambda_i/\hbar + i\varepsilon}. \qquad (4)$$

The absorption coefficient is given by

$$\text{Im}\chi(\hbar\omega) = \sum_{i=1}^{4} A_i \frac{\Gamma}{(\hbar\omega - \lambda_i)^2 + \Gamma^2}. \qquad (5)$$

The eigenvalues are

$$\lambda_{1,2} = \tfrac{1}{2}\{(a + \hbar\omega_e + \alpha) \pm [(a + \hbar\omega_e + \alpha)^2$$
$$- 4(\omega_e(a + \alpha) - 4t^2)]^{1/2}\},$$

$$\lambda_{3,4} = \tfrac{1}{2}\{(a' + \hbar\omega_e + \alpha) \pm [(a' + \hbar\omega_e + \alpha)^2$$
$$- 4(\omega_e(a' + \alpha) - 4t^2)]^{1/2}\}. \qquad (6)$$

The eigenvalues are the resonance energies of the absorption spectrums. The amplitudes A_1–A_4 are complicated, and not given explicitly here. The infinitesimal number ε is replaced by a phenomenological broadening half-width Γ. Lasing threshold is defined as the pumping level beyond which the absorption coefficient Im χ is negative for some frequency range.

The effect of pumping on the absorption coefficient comes in through the Q dependency of $\hbar\omega_e$, α and t. Q, in turn, depends on the quasi-particle concentrations n_e and n_x. In the continuum model [10], the excitons and excimers are both one-dimensional electron–hole bound states. The only difference is that the electron and hole are in the same chain for excitons, while they are not for excimers. Their binding energies are determined by the cut-off of Coulomb potential energy [10,11]. For excitons, the cut-off is equal to the coherence length ξ of the SSH model. For excimers, the cut-off is approximately equal to $\sqrt{\xi^2 + Q^2}$. More explicitly, the binding energies satisfy [11]

$$\frac{E_g - \hbar\omega_e}{E_g - \hbar\omega_x} = \frac{\alpha^2(\xi/a_B^*)}{\alpha^2((\sqrt{\xi^2 + Q^2})/a_B^*)}.$$

$\alpha(x)$ is the solution of the equation $\log(2x/\alpha) + \tfrac{1}{2}\alpha = 0$. E_g is the band gap. a_B^* is the Bohr radius, which is approximately equal to the size of the exciton wave function. For PPV, we take $\xi = 1.95c$, with the lattice constant c equal to 6.54 Å, and $a_B^* = \xi/0.3$ [12]. E_g is 2.8 eV and E_x is 2.3 eV. The Q-dependencies of interchain coupling constants α and t are assumed to be of the form $\alpha(Q) = \alpha_0 \exp(-Q/\sigma)$ and $t(Q) = t_0 \exp(-Q/\sigma)$. σ is the lateral size of the p_z orbital of the π-electrons, and is taken to be 1.4 Å. α_0 and t_0 are assumed to be determined by the side groups, and will be specified later as adjustable parameters. $\hbar\beta$ can be written as $f E_x a_B^*/L$, where $L = Nc$ is the length of the chain [8]. N is the number of units in each chain, and is taken to be 10. f is a numerical factor which will be adjusted later. The spring constant K in the potential energy U, due to side group compression, is written as $K = Nk$, where k is the spring constant per monomer. k is also determined by the choice of the side groups, and will be specified later. Q_0 is taken as 7.5 Å.

We first present our results in the case where, with strong pumping, the effect of the interchain coupling is substantial. The absorption coefficient is calculated for increased values of $n_t \equiv n_e + n_x$, the total number of quasi-particles. We choose the fixed ratio n_e/n_t 0.9, according to the observation that excimers are the predominant species after excitations. Referring to Eq. (5), the absorption Im χ is the summation of four Lorentzians, with amplitudes A_1–A_4 and resonance energies λ_1–λ_4. In Figs. 1(a) and (b), we show the amplitudes and the resonance energies as functions of n_t. $Q(n_t)$ is also shown in the inset. For smaller n_t, the interchain coupling is negligible. The nearly degenerate λ_1 and λ_3 represents the excimer creation energy. λ_2 and λ_4 are the exciton resonances, split due to the exciton self-interactions. The decrease of the excimer energy causes PA that gets spectrally close to the exciton energy. For larger n_t, excitons and excimers are mixed and four resolved energies show up with mixed identities. The important result here is that while the energies get more and more separated, A_3 and A_4 get more and more negative, which signals gain. In Figure 2(a), we show the corresponding absorption spectrum for various level of pumping. The dotted line is the zero for each
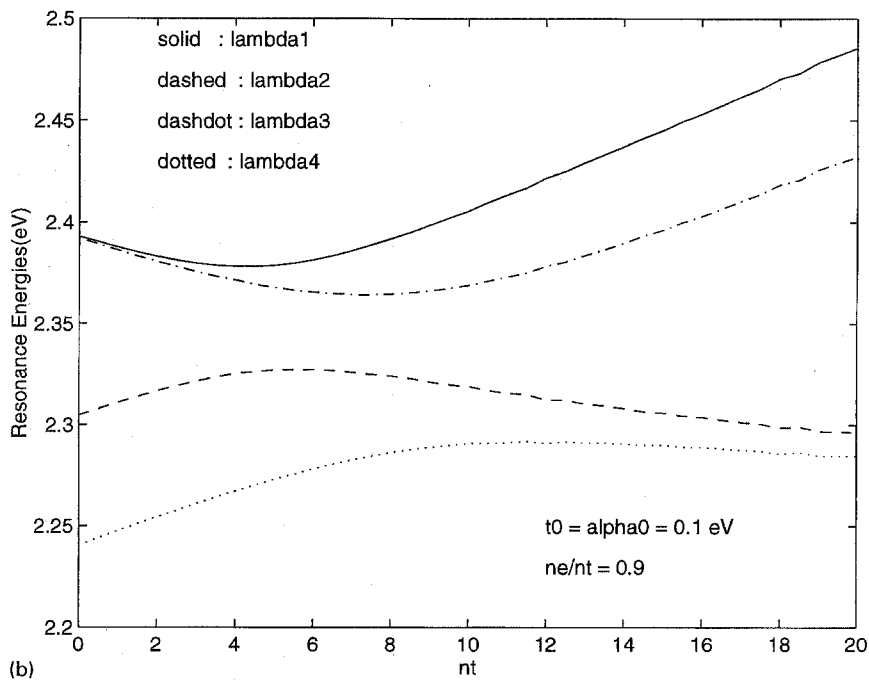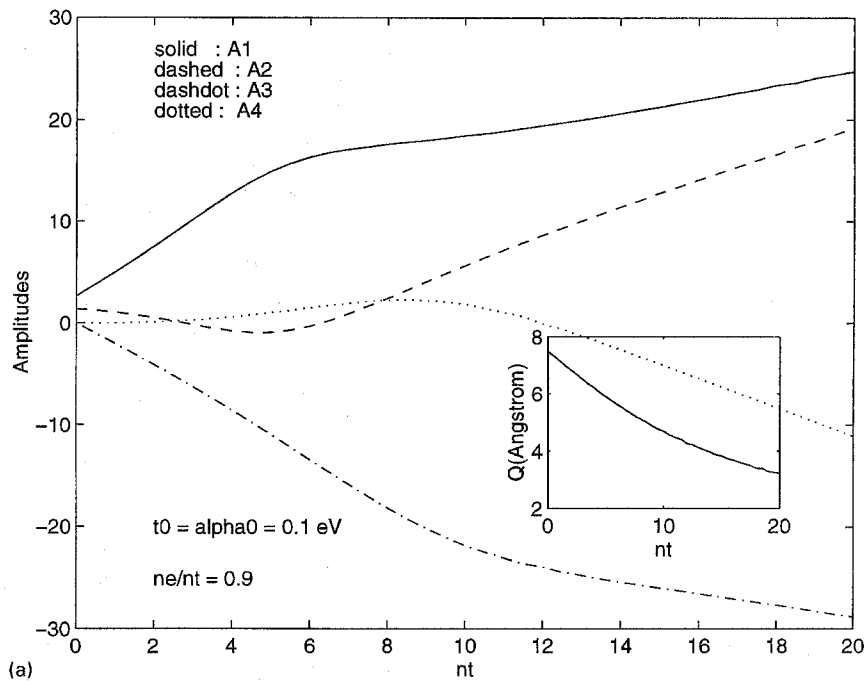
(a)

(b)

Fig. 1. The amplitudes and resonances energies (see Eq. (5)) for the absorption spectrum are plotted as functions of total number of quasi-particles n_t. The inset shows the interchain distance changes. The scale for the amplitudes is arbitrary. The interchain coupling constants t_0 and α_0 are equal to 0.1 eV. $\hbar g_e$ and $\hbar g_x$ are chosen to be equal. $f = 0.1$, $k = 0.01$ eV/Å.
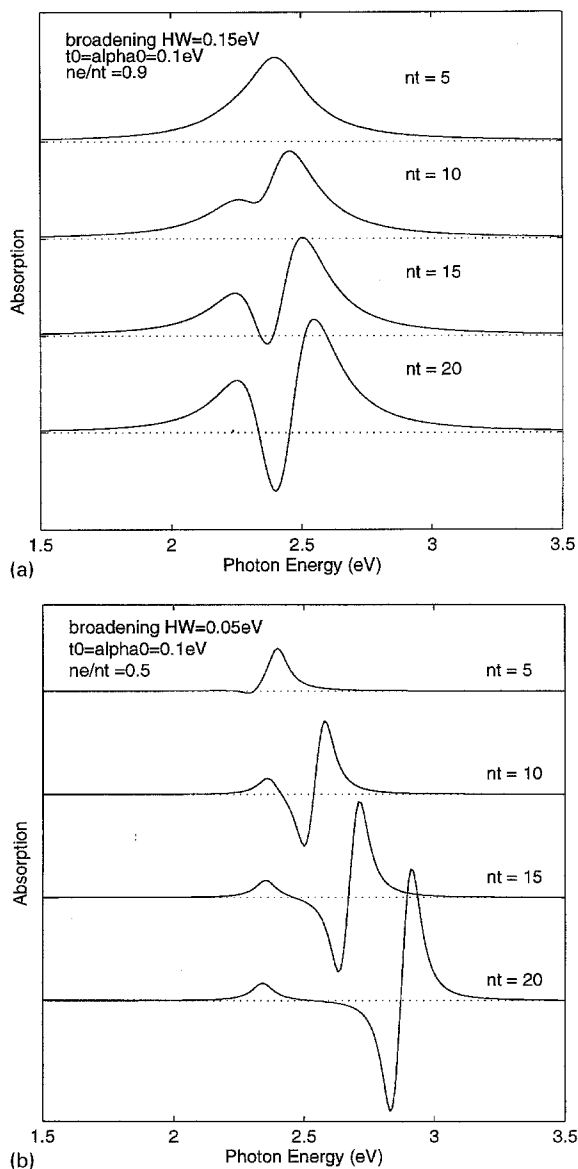
Fig. 2. The absorption spectrum for various n_t, the total number of quasi-particles: (a) $n_e/n_t = 0.9$, $\Gamma = 0.15$ eV, gain (negative absorption) occurs for n_t larger then about 15; (b) $n_e/n_t = 0.5$, $\Gamma = 0.05$ eV, gain (negative absorption) occurs for n_t larger then about 5. Dotted line is the zero for each spectrum.

spectrum. Choosing the Lorentzian half-width Γ to be 0.15 eV, one sees that the gain threshold is reached when n_t is about 15. A deep gain spectral region near 2.4 eV is clear as n_t reaches 20. For samples

with 2.68×10^{-22} cm^3 unit cell containing two monomers [12], the corresponding quasi-particle concentration is 1.1×10^{22} cm^{-3}. In Fig. 2(b), we show the absorption spectrum for $\Gamma = 0.05$ eV and $n_e/n_t = 0.5$. Gain is reached for n_t around 5, mainly due to smaller Γ. The corresponding quasi-particle concentration is 3.7×10^{21} cm^{-3}. We compare this results with the recent experimental data on stimulated emission by Wei et al. [13]. They found that the differential transmission $\Delta T/T$ is 10^{-3} when quasi-particle density n is 10^{16} cm^{-3}. In order to achieve net gain, the transmission $\Delta T + T$ has to be larger than one (negative absorption). Therefore, the gain condition becomes $\Delta T/T = 1/T - 1$. Assuming that ΔT is always proportional to n, the required n becomes $10^{19}(1/T - 1)$ cm^{-3}. For typical experiments with $T \simeq 0.1$ [3], this density is about 10^{20} cm^{-3}, which is only one order of magnitude smaller than our result. This difference is probably because our result is based on lattice constants of PPV crystal [12], while Wei measures DOOPPV, whose side group is much larger than the one in PPV, and their backbones presumably more separated. Since we consider excitations on the backbones only, the corresponding n in DOOPPV should be somewhat smaller than in PPV, consistent with the above estimates.

When the interchain coupling constants t_0 and α_0 are zero, no gain is present before $n_t = 20$, if Γ is still 0.15 eV. The amplitudes and resonances are shown in Figs. 3(a), and (b). There are only three of them due to degeneracy. λ_1 is the excimer energy, and note that its amplitude A_1 remains a positive constant. Therefore, from Fig. 3(b), the creation of excimers always causes a PA, which becomes spectrally overlapped with the exciton resonances λ_2, λ_3, and overwhelms gain due to excitons. In this case, a net gain is possible only when n_x itself is large enough to overcome the PA, which, given the small ratio $n_x/(n_t(=0.1)$, means an even larger n_t. Our model may not be applicable for such highly excited states.

In summary, for small interchain couplings t_0 and α_0, gain is unlikely if the excimers are the predominant quasi-particles. However, for larger t_0 and α_0, gain can be achieved as we increase the pumping level, no matter what the ratio n_e/n_x is. In addition, because $\hbar\omega_e$ is not a sensitive function of
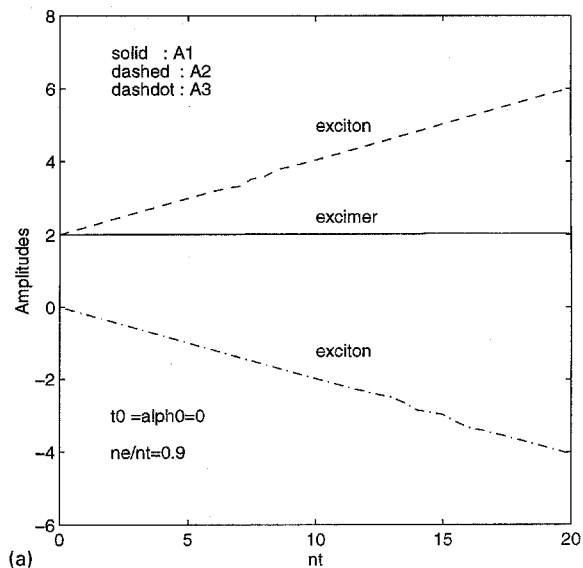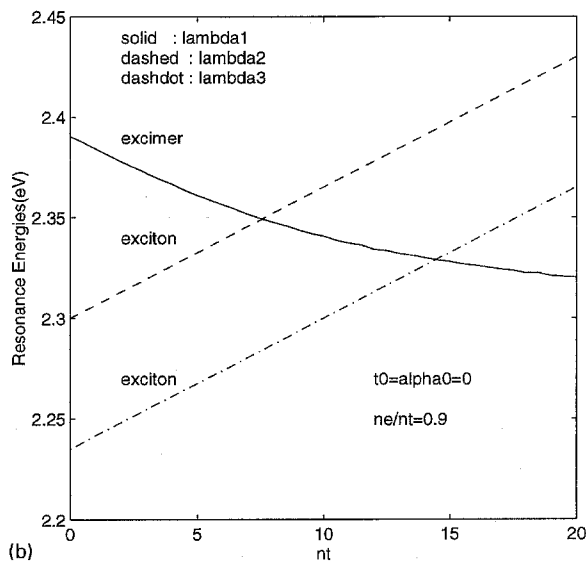
Fig. 3. The amplitudes and resonances energies for the absorption coefficient are shown for $t_0 = \alpha_0 = 0$. Other parameters are the same as Fig. 1.

Q, a "soft" spring constant $k(\sim 0.01$ eV per unit) is required to achieve a significant decrease of Q with pumping. We believe that polymers with π-electrons laterally delocalized into the side groups are more likely to satisfy this requirements for lasing. In this model, the lattice dynamics is not considered. As a first approximation, this can be justified because the lattice distortion within each chain is substantially reduced in the presence of interchain coupling [12]. A more microscopic treatment of the dynamics of conducting polymer under pumping, including the lattice degree of freedoms, is under current investigation.

References

[1] D. Moses, Appl. Phys. Lett. 60 (1992) 3215.
[2] M. Yan et al., Phys. Rev. Lett. 72 (1994) 1104.
[3] M. Yan et al., Phys. Rev. B 49 (1994) 9419.
[4] E. Conwell, H. Mizes, Phys. Rev. B 51 (1994) 6953; ibid 50 (1994) 11243; G. Hayes et al., Phys. Rev. B 52 (1995) R11569.
[5] J. Michl, V. Bonacic-Koutecky, Electronic Aspects of Organic Photochemistry, Wiley, Toronto, 1990.
[6] G. Mahan, Many-particle Physics, Plenum Press, New York, 1981.
[7] E. Hanamura, J. Phys. Soc. Japan 29 (1970) 50.
[8] N. An, Phys. Rev. B 48 (1993) 11732.
[9] G. Agarwal, Phys. Rev. A 51 (1995) R2711.
[10] S. Abe, J. Phys. Soc. Japan 58 (1989) 62.
[11] R. Loudon, Am. J. Phys. 27 (1959) 649.
[12] P. da Costa, R. Dandrea, E. Conwell, Phys. Rev. B 47 (1993) 1800.
[13] X. Wei, S. Frolov, Z. Vardeny, Synt. Met. 78 (1996) 295.