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In-gap polaritons in uniformly filled microcavities

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Abstract

We examine the nature and the dispersion of new polariton modes, which appear in the polariton gap (i.e. within the Rabi splitting), considering the spectrum of polaritons in a planar microcavity uniformly filled with a resonant material and exhibiting the strong exciton–photon coupling regime. These additional modes are the consequence of the quantization of the excitonic states caused by the confinement. We consider these in-gap modes in materials typically used in microcavities and link the obtained results to experiments, where such in-gap states have indeed been observed. We show that the splitting between the in-gap modes and their bandwidth depend on the bandwidth of the exciton out of the microcavity and on the oscillator strength of the excitonic transition.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Planar semiconductor microcavities are known to enhance and control the interaction between light and electronic excitations in solids [1]. If the empty cavity mode is in resonance with the excitonic transition of the material placed in the microcavity and the exciton–photon coupling is strong enough in comparison with the losses, the eigenstates of such a system are mixed exciton–photon states called cavity polaritons. Such a situation is known as the strong coupling regime. The formation of polaritons is manifested near the resonance between the uncoupled exciton and the cavity photon by the opening of a gap in the excitation spectrum (the so-called vacuum Rabi splitting).

During the last decade much attention has been devoted to the study of microcavities filled by an organic material, which acts as a resonant medium. The interest is motivated by the considerably larger Rabi splitting energies and the stability of polaritons at room temperature. A variety of filling materials, from amorphous disordered J aggregates of cyanine dyes [2] to single crystals of anthracene [3, 4] are available at the moment. Also, organic microcavities have the advantage of a larger active thickness, as the whole volume of the cavity is filled by a resonant material. As a reminder, in most inorganic samples, a thin quantum well with a Wannier–Mott exciton is placed in the middle of the microcavity; the quantum well confinement increases the exciton oscillator strength, but the price to pay is a smaller exciton–photon real space overlap.

The finite cavity width leads to the quantization of the empty cavity modes in the growth direction (z -axis), so that the eigenstates form a set of modes characterized by different k_z . The thickness of the cavity, $L \sim 1000 \text{ \AA}$, is chosen in such a way that the lowest cavity mode is tuned to a resonance with the exciton energy $\hbar\omega_T \sim 2 \text{ eV}$. In the approximation of ideal mirrors, $k_z = k_m = \pi m/L$. The higher- m empty cavity modes are separated by an energy $\hbar c\pi/L\sqrt{\epsilon_c} \sim 2 \text{ eV}$ from the resonance region. As the typical Rabi splitting energies range from a few to tens of meV for semiconductor microcavities, and from tens to several hundreds of meV for organic microcavities, these higher-energy modes are customarily excluded from consideration, and the problem reduces to the interaction between the exciton and the photon mode with the smallest possible value of k_z ($m = 1$).

However, the neglect of higher- m modes is substantiated only in the case of usual inorganic microcavities, and can fail when dealing with a microcavity uniformly filled with a resonant material. In this latter case, the excitonic component is also quantized in z -direction. Below we show that, while the empty cavity modes with higher m are well separated from the resonance region, the excitonic states with higher m typically still have energies around $\hbar\omega_T$. The interaction between the excitons and photons with $m > 1$ is non-resonant, and thus the account of the retardation effects for these m can lead only to small (in comparison with the Rabi splitting) shifts of bare exciton states. However a small admixture of light acquired

by these states via a non-resonant interaction with the empty cavity modes with the same k_z can assist their emission from the polariton gap.

In this paper we show that there can be two different mechanisms of formation of these states. The first is applicable to materials with a small effective mass of excitons. An example is an inorganic semiconductor, such as GaAs. In such a material the confinement leads to the formation of a set of bare exciton subbands, each subband characterized by a different k_z . The account of retardation results in small shifts of these subbands. The second mechanism works in materials with a weak intermolecular interaction, where the exciton bandwidth is small. An example is a molecular crystal, such as anthracene. As a limiting case let us consider a material with such a narrow exciton band that one can completely neglect intermolecular interaction. Then qualitatively we can describe the situation as follows. Different higher- m empty cavity modes interact with one and the same electronic transition ω_T . Each empty cavity mode induces an excitonic polarization with the same m in the resonant material. The interaction between the empty cavity mode and the induced polarization with the same m leads to an m -dependent shift of the resulting polaritonic states from ω_T . The dependence of the shift on m appears because the strength of the interaction depends on the energy separation between the empty cavity mode and ω_T , and thus decreases with the growth of m . Thus, both mechanisms result in the appearance of low-energy exciton-like polaritonic bands $\omega_L(m; k)$, but in the first case the light–matter interaction results in further shifts of originally resolved excitonic bands, while in the second case the bands get resolved due to the retardation effects only. The in-gap polaritons formed by the first mechanism have been observed many years ago in a GaAs microcavity of an unusual inorganic microcavity structure (instead of a quantum well in the middle, all the space between the mirrors was continuously filled by GaAs) [5]. The in-gap polaritons formed by the second mechanism have been observed very recently in a microcavity filled by a monocrystal of anthracene [4].

These in-gap states were overlooked in most previous discussions and for this reason their nature has never been properly discussed. These states are particularly important for organic microcavities, as in these nanostructures typically all the space between the mirrors is filled by a resonant material. Even if these states are not directly visible in the gap (for instance, if they are situated within the absorption band), they are present as dark states and can play an important role in the relaxation processes.

The majority of organic structures are optically anisotropic. Many of them (such as anthracene) have a layered structure and in a good approximation can be characterized by a diagonal dielectric tensor. For this reason in this paper we derive the dispersion equation for in-gap polaritons in a microcavity uniformly filled by a crystal with a diagonal dielectric tensor. This approximation will allow us to discuss the most typical particular cases of resonant materials used in microcavities, such as a cubic semiconductor crystal with a Wannier–Mott exciton, as well as J aggregates and anthracene-type monocrystals with Frenkel excitons.

2. Cavity polaritons in a medium with a diagonal dielectric tensor

Let us consider a microcavity of thickness L uniformly filled by a material with excitonic resonances. The presence of the resonances will be taken into account in the components of the dielectric tensor. In general (see [6], chapter IV),

$$\varepsilon_{ij}(\omega, \mathbf{k}, k_z) = \varepsilon_c \delta_{ij} - \frac{8\pi}{v\hbar} \sum_{\alpha} \frac{P_i^{\alpha} P_j^{\alpha} \omega_{\alpha}(0)}{\omega^2 - \omega_{\alpha}^2(\mathbf{k}, k_z)},$$

$$i = x, y, z, \quad (1)$$

where the sum is taken over all the excitonic resonances, $\omega_{\alpha}(\mathbf{k}, k_z)$ and $\mathbf{P}^{(\alpha)}$ are, respectively, the α th excitonic transition energy and the exciton transition dipole moment, \mathbf{k} is the in-plane wavevector, v is the volume of the unit cell of the crystal, and ε_c is the background dielectric constant. As any symmetric tensor, the dielectric tensor can be reduced to a diagonal form. In all cases considered below, due to the symmetry properties of the crystal, in the coordinate system coinciding with the principal axes of the dielectric tensor its components take the following form [7]:

$$\varepsilon_{ii}(\omega, \mathbf{k}, k_z) = \varepsilon_c \left(1 - \frac{W_i^2}{\omega^2 - \omega_i^2(\mathbf{k}, k_z)} \right), \quad i = x, y, z, \quad (2)$$

where the constants $W_i^2 = 8\pi P_i^2 \omega_i / v\hbar \varepsilon_c$ are proportional to the oscillator strength of the excitonic transition. The dependence of $\omega_i(\mathbf{k}, k_z)$ on the wavevector corresponds to the account of the spatial dispersion of the medium. The anisotropy means that different components of the dielectric tensor can be different.

Let us assume for simplicity that the microcavity has ideal mirrors, so that the boundary condition is the vanishing of the tangential component of the electric field at $z = \pm L/2$. Then the eigenmodes will be characterized by $k_z = k_m = m\pi/L$, and the z -dependence of the modes will have an alternating symmetry: the modes with odd (even) m will behave as $\cos k_m z$ ($\sin k_m z$). Solving the Maxwell equations with a diagonal dielectric tensor with arbitrary diagonal elements $\varepsilon_{xx}(\omega, \mathbf{k}, k_z)$, $\varepsilon_{yy}(\omega, \mathbf{k}, k_z)$ and $\varepsilon_{zz}(\omega, \mathbf{k}, k_z)$, we obtain the following dispersion equation for the m th mode:

$$\left[\left(\frac{\omega^2}{c^2} \varepsilon_{zz}^{(m)} - k^2 \right) \varepsilon_{xx}^{(m)} - k_m^2 \varepsilon_{zz}^{(m)} \right] \left[\frac{\omega^2}{c^2} \varepsilon_{yy}^{(m)} - k^2 - k_m^2 \right] \cos^2 \varphi$$

$$+ \left[\left(\frac{\omega^2}{c^2} \varepsilon_{zz}^{(m)} - k^2 \right) \varepsilon_{yy}^{(m)} - k_m^2 \varepsilon_{zz}^{(m)} \right]$$

$$\times \left[\frac{\omega^2}{c^2} \varepsilon_{xx}^{(m)} - k^2 - k_m^2 \right] \sin^2 \varphi = 0, \quad (3)$$

where φ is the angle between x -axis and the direction of the in-plane wavevector \mathbf{k} , and $\varepsilon_{ii}^{(m)} = \varepsilon_{ii}(\omega, \mathbf{k}, k_m)$. This dispersion equation for $m = 1$ has been obtained in [8], where the details of the derivation can be found, and the generalization on the case of arbitrary m is straightforward. Below we examine this dispersion equation for three particular symmetries of the filling material.

2.1. Cubic crystal

Let us consider as a first example a cubic crystal with spatial dispersion. This model corresponds, for instance, to a microcavity uniformly filled by an inorganic semiconductor, such as the sample of [5]. As known, inorganic semiconductors possess Wannier–Mott excitons with a large radius and wide bands characterized by an effective mass, which can be an order of magnitude smaller than the effective mass of a Frenkel exciton in a molecular crystal. For a cubic crystal $\varepsilon_{ii}(\omega, \mathbf{k}, k_z = k_m) = \varepsilon^{(m)}(\omega, k)$ for all i . Then the dispersion equation for transversal polaritons (3) reduces to the familiar form:

$$\frac{\omega^2}{c^2} \varepsilon^{(m)}(\omega, k) = k^2 + k_m^2. \quad (4)$$

Here $\varepsilon^{(m)}$ is given by equation (2) with $\omega_i(\mathbf{k}, k_z = k_m) \equiv \omega_T(m; k)$. In the effective mass approximation $\omega_T(m; k) = \omega_T + (\hbar/2M_*)[k^2 + k_m^2]$ (here M_* is the exciton effective mass). For $m = 1$ equation (4) describes conventional cavity polaritons considered previously in many works. Larger values of m on the right-hand side would require on the left-hand side either larger values of ω (corresponding to higher- m empty cavity modes with the energy separation about 2 eV), or larger values of ε (higher- m bare exciton modes). Equation (4) can be rewritten in a customary form

$$[\omega^2 - \omega_{\text{cav}}^2(m; k)][\omega^2 - \omega_T^2(m; k)] = \omega^2 W^2, \quad (5)$$

where the dispersion of the m th empty cavity photon $\omega_{\text{cav}}(m; k) = c\sqrt{(k^2 + k_m^2)/\varepsilon_c}$ and the dispersion of the m th bare exciton $\omega_T(m; k) = [\omega_T + \hbar\pi^2 m^2/2L^2 M_*] + \hbar k^2/2M_*$ are introduced. The modes $\omega_T(m; k)$ have a parabolic dispersion. The energy separation $\hbar\pi^2 m^2/2L^2 M_*$ between them is inversely proportional to the effective mass of the exciton, so that it is clear that the splitting between these modes is the result of the dependence of the exciton energy on the wavevector. The separation grows quadratically in m . The solutions of equation (5) for $m > 1$ are doublets with the upper branch almost coinciding with $\omega_{\text{cav}}(m; k)$ and with the lower branch (the in-gap polaritons) with a dispersion given by

$$\omega_L(m > 1; k) = \omega_T(m; k) - \frac{W^2 \omega_T(m; k)}{2[\omega_{\text{cav}}^2(m; k) - \omega_T^2(m; k)]}. \quad (6)$$

The energies of the in-gap polaritons are sums of the m th bare exciton dispersion $\omega_T(m; k)$ and the polaritonic correction, which vanishes with the growth of m . As expected, the polaritonic correction also vanishes in the limit $c \rightarrow \infty$ (because $\omega_{\text{cav}}(m, k) \propto c$). The dispersion of these modes is shown in figure 1 for the parameters of a GaAs microcavity: $\varepsilon_c = 9$, $\hbar W = 3$ meV, the detuning $u = \omega_{\text{cav}}(m = 1, k = 0) - \omega_T = 0$, $M_* = 0.3m_e$ (m_e is the electron mass). Each mode is marked by its value of m . The exciton-like polariton modes with almost parabolic dispersion are clearly seen in the polariton gap. These are the modes observed in the experiment [5] as extra emission peaks situated within the polariton gap (the Rabi splitting) and correctly interpreted as the result of quantization of the exciton center of mass motion. The modes with $m \geq 5$ are resonant with the upper polariton

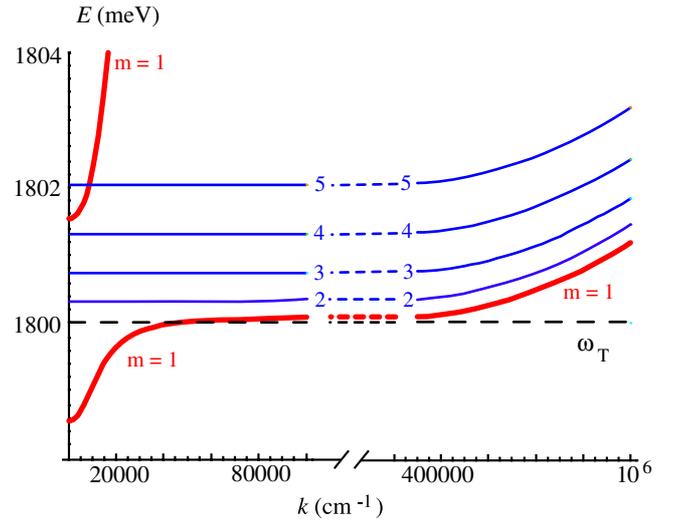


Figure 1. Dispersion of conventional cavity polaritons ($m = 1$, thick lines) and the in-gap modes with $m = 2-5$ (thin lines) for a cubic crystal. The parameters of GaAs are used for the plot (small effective mass of the exciton, small oscillator strength of the exciton transition).

band. They have a very small admixture of light and thus are expected to be dark. We stress that here the large (as a fraction of the Rabi splitting) separation between these modes is due to the small effective mass of the Wannier–Mott exciton.

2.2. Uniaxial crystal

A uniaxial crystal is described by a dielectric tensor with the components $\varepsilon_{xx} = \varepsilon_{yy} \equiv \varepsilon_{\parallel}$. For example, a microcavity filled with J aggregates with all the dipole transitions lying in the microcavity plane [2] can be considered as a uniaxial crystal in a zero-order approximation with respect to disorder. For this choice of the components (3) splits into two equations:

$$\frac{\omega^2}{c^2} \varepsilon_{\parallel} = k^2 + k_m^2, \quad \frac{\omega^2}{c^2} = \frac{k^2}{\varepsilon_{zz}} + \frac{k_m^2}{\varepsilon_{\parallel}}, \quad (7)$$

and the first (second) equation corresponds to the TE (TM)-modes (the first and second modes are also known, respectively, as ordinary and extraordinary waves). Having in mind a microcavity filled by J aggregates of cyanine dyes [2], we assume that $\varepsilon_{\parallel}(\omega)$ has the form (2), but with the resonance frequency ω_T independent of the wavevector: the mean distance between J aggregates is about 200 Å, and one can consider them as non-interacting point dipoles. Then with $\varepsilon_{zz} = \varepsilon_c$ the dispersion equations (7) can be rewritten as

$$[\omega^2 - \omega_{\text{cav}}^2(m; k)][\omega^2 - \omega_T^2] = \omega^2 W^2, \quad (8)$$

$$[\omega^2 - \omega_{\text{cav}}^2(m; k)][\omega^2 - \omega_T^2] = W^2 \left(\omega^2 - \frac{c^2 k^2}{\varepsilon_c} \right).$$

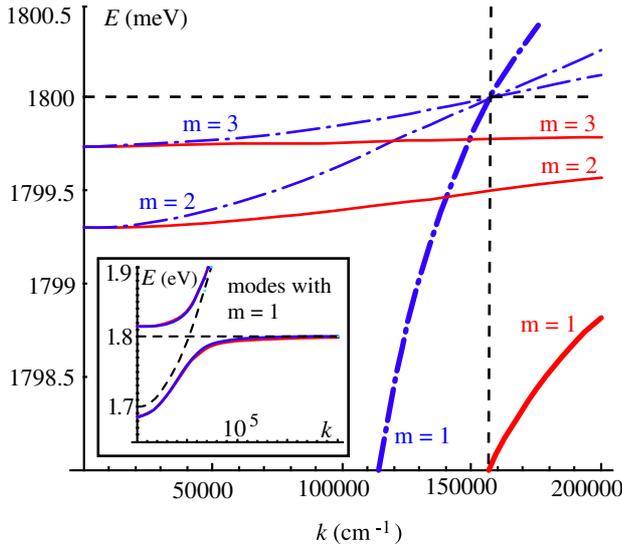


Figure 2. Dispersion of lower polaritons with $m = 1 - 3$ near the resonance frequency for a uniaxial crystal with $\omega_T = \text{const}$ and moderate oscillator strength of the electronic transition (as for J aggregates of cyanine dyes). TE (TM) modes are shown by solid (dot- and-dash) lines. Inset: conventional cavity polaritons with $m = 1$.

The solutions with $m = 1$ correspond to the conventional polariton modes (shown in the inset of figure 2). For them a slight difference in the dispersion of TE and TM modes appear at larger k . Again, each of equations (8) with $m > 1$ has two solutions, the upper branch almost coinciding with $\omega_{\text{cav}}(m; k)$, and the lower branch having the dispersion

$$\begin{aligned} \omega_L^{\text{(TE)}}(m > 1; k) &= \omega_T - \frac{W^2 \omega_T}{2[\omega_{\text{cav}}^2(m; k) - \omega_T^2]}, \\ \omega_L^{\text{(TM)}}(m > 1; k) &= \omega_T - \frac{W^2(\omega_T^2 - c^2 k^2 / \epsilon_c)}{2\omega_T[\omega_{\text{cav}}^2(m; k) - \omega_T^2]}, \end{aligned} \quad (9)$$

which is a sum of the electronic transition frequency of J aggregates (dispersionless and the same for all m , as ω_T does not depend on the wavevector) and a polaritonic correction. These modes are shown in figure 2 for $m = 2, 3$ and the parameters corresponding to a microcavity filled by J aggregates of cyanine dyes: the Rabi splitting $\hbar W = 80$ meV, $\epsilon_c = 3$ and with the detuning $\hbar u = -100$ meV. The figure shows the zoom of the region around ω_T . The continuous (dot- and-dash) lines denote TE- (TM-) polarized modes, the horizontal dashed line denotes the resonance energy $\hbar\omega_T$. The vertical dashed line marks the wavevector $k_T = \omega_T \sqrt{\epsilon_c} / c$ at which all the TM modes intersect (see (9)). The appearance of this intersection can be understood by taking into account the relation between the in-plane and the normal component of the electric field in the TM mode

$$E_1(z) = \frac{i\epsilon_c}{k\epsilon_{\parallel}(\omega)} \frac{\partial E_z(z)}{\partial z}, \quad (10)$$

which can be found from the Maxwell equations (see [8]). This relation is true for all m . From this relation it is clear that at $\omega = \omega_T$, where $\epsilon_{\parallel}(\omega) \rightarrow \infty$, the in-plane (longitudinal)

component of the electric field vanishes, and the total electric field is directed normally to the mirrors. This field does not interact with the excitonic transition, which is polarized in the microcavity plane, and the polaritonic correction vanishes for any m .

To summarize, in the case considered here with $\omega_T = \text{const}$ the separation between the modes (9) appears only as a result of a non-resonant interaction between the higher-energy empty cavity modes and the electronic transition at ω_T . The closeness of the modes with $m > 1$ to ω_T and to each other (the maximal separation is less than 1 meV) is a result of the relatively weak oscillator strength of the electronic transition in J aggregates: as follows from (9), this separation is $\sim W^2 / \omega_T$. It means that for J aggregates the wavevector dependence of the energy of these in-gap polaritons cannot be directly observed: indeed, these states are exciton-like and thus should have an inhomogeneous linewidth ~ 50 meV. As we show in the next section, larger values of W also lead to formation of well-resolved bands in the case $\omega_T = \text{const}$.

2.3. Biaxial crystal

Let us consider a microcavity filled by a monocrystal of a linear polyacene, such as anthracene, naphthalene, tetracene or pentacene. As known, due to the resonant intermolecular Coulomb interaction, the excitonic band is split into as many Davydov components as there are inequivalent molecules in the unit cell. The unit cells of these crystals contain two molecules with the same excitation energy but with two differently oriented transition dipole moments, \mathbf{p}_1 and \mathbf{p}_2 . Then due to intermolecular interaction two excitonic bands appear, and the dipole moments of the components of the doublet for small wavevectors are: $\mathbf{P}_b = \mathbf{p}_1 + \mathbf{p}_2$, $\mathbf{P}_a = \mathbf{p}_1 - \mathbf{p}_2$, with $\mathbf{P}_b \perp \mathbf{P}_a$ [9]. Choosing the axis x and y along \mathbf{P}_b and \mathbf{P}_a , one can write the dielectric tensor of such a crystal in the form [7]

$$\begin{aligned} \epsilon_{xx} &= \epsilon_c \left[1 - \frac{W_b^2}{\omega^2 - \omega_b^2} \right], & \epsilon_{yy} &= \epsilon_c \left[1 - \frac{W_a^2}{\omega^2 - \omega_a^2} \right], \\ \epsilon_{zz} &= \epsilon_c, \end{aligned} \quad (11)$$

where $\omega_{a,b}$ are the energies of the components of the Davydov doublet (which can be considered either as dispersionless or as wavevector dependent). Here we again neglect the small off-diagonal terms ϵ_{xz} and ϵ_{zx} , which exist in anthracene. Substituting (11) into (3) one can show that the dispersion equation can be written as

$$\begin{aligned} &[\omega^2 - \omega_{La}^2(m; \mathbf{k})][\omega^2 - \omega_{Ua}^2(m; \mathbf{k})][\omega^2 - \omega_{Lb}^2(m; \mathbf{k})] \\ &\times [\omega^2 - \omega_{Ub}^2(m; \mathbf{k})] = W_a^2 W_b^2 \frac{c^4 k_x^2 k_y^2}{\epsilon_c^2}, \end{aligned} \quad (12)$$

where

$$\omega_{La,Ua}^2(m; \mathbf{k}) = \frac{1}{2} \left\{ \omega_{\text{cav}}^2(m; k) + \omega_a^2 + W_a^2 \mp \sqrt{(\omega_{\text{cav}}^2(m; k) - \omega_a^2 - W_a^2)^2 + 4W_a^2 \left(\omega_{\text{cav}}^2(m; k) - \frac{c^2 k_y^2}{\varepsilon_c} \right)} \right\}, \quad (13)$$

$$\omega_{Lb,Ub}^2(m; \mathbf{k}) = \frac{1}{2} \left\{ \omega_{\text{cav}}^2(m; k) + \omega_b^2 + W_b^2 \mp \sqrt{(\omega_{\text{cav}}^2(m; k) - \omega_b^2 - W_b^2)^2 + 4W_b^2 \left(\omega_{\text{cav}}^2(m; k) - \frac{c^2 k_x^2}{\varepsilon_c} \right)} \right\}.$$

As the crystal is optically anisotropic in the cavity plane, the eigenmodes cannot be classified as purely TE- or TM-polarized modes (except for the waves propagating along the optical axes of the crystal). In equation (12) the eigenmodes are represented as two doublets of polaritons, each doublet attributed to either the a or b exciton, and the right-hand side (vanishing along the optical axes of the crystal) determines the mixing between these modes. The dispersion of cavity polaritons in a crystal with two molecules in a unit cell was studied theoretically for the first time in [8], but in this work higher- m modes were not discussed. It has been shown that in spite of the strong optical anisotropy of the crystal, the spectra of cavity polaritons are isotropic at small wavevectors and a weak anisotropy only appears at larger k . This is a combined effect of the special arrangements of the fields in the modes and of the reduced dimensionality of the problem. First, the electric field in the microcavity is such a combination of TE- and TM-polarized empty cavity photons that the total electric field in a polariton mode is parallel to the excitonic transition dipole moment for each given \mathbf{k} , and this removes the dependence of the Rabi splitting energy on the direction of \mathbf{k} . Second, the non-analytical dependence of the exciton energy on its wavevector existing in bulk anisotropic crystals at vanishing k [9] does not appear, as in two dimensions the dipole sums converge at small k . The complete discussion of this weakening of the anisotropy of the spectra can be found in [8]. So here we do not fix our attention on the examination of the angle dependence of the energy of the modes, and give just several examples with the focus made on the modes with higher values of m . The dispersion of these modes can be found from (12). For each m there are two upper modes with their energies almost coinciding with $\omega_{\text{cav}}(m; k)$ and with mutually perpendicular polarizations, and two lower modes with mutually perpendicular polarizations, one lower mode attributed to a -exciton, the other to b -exciton. These lower modes have the following dispersion equation:

$$\omega_A(m, \mathbf{k}) = \omega_a - \frac{W_a^2 A(\omega, \mathbf{k})}{2\omega_a [\omega_{\text{cav}}^2(m, k) - \omega_a^2]}, \quad (14)$$

$$\omega_B(m, \mathbf{k}) = \omega_b - \frac{W_b^2 B(\omega, \mathbf{k})}{2\omega_b [\omega_{\text{cav}}^2(m, k) - \omega_b^2]},$$

where the second terms again describe the non-resonant

polaritonic effect, and

$$A(\omega, \mathbf{k}) = \left(\omega_a^2 - \frac{c^2 k_y^2}{\varepsilon_c} \right) - \frac{W_b^2 k_x^2 k_y^2 c^4 / \varepsilon_c^2}{(\omega_a^2 - \omega_b^2) [\omega_{\text{cav}}^2(m, k) - \omega_b^2]},$$

$$B(\omega, \mathbf{k}) = \left(\omega_b^2 - \frac{c^2 k_x^2}{\varepsilon_c} \right) + \frac{W_a^2 k_x^2 k_y^2 c^4 / \varepsilon_c^2}{(\omega_a^2 - \omega_b^2) [\omega_{\text{cav}}^2(m, k) - \omega_a^2]}. \quad (15)$$

Experimental studies of microcavities with an organic crystalline material are in an initial stage [3, 4]. In particular, in [4] multiple polariton modes situated close to the resonance frequencies have indeed been observed and were interpreted as higher- m modes. We believe that these modes are exactly the ones which we consider here.

In figure 3(a) we show for reference the polariton modes with $m = 1$ for $\varphi = 0$ (φ is the angle between x -axis and the direction of the wavevector \mathbf{k}). The modes with polarization along \mathbf{P}_b (\mathbf{P}_a) are shown as solid (dash- and-dot) lines. The detuning is chosen large and negative: $\hbar u = -300$ meV. The two excitonic resonances and the empty cavity modes are shown as thin dashed lines. We use the following numbers taken from [4]: $\omega_b = 3122$ meV, $\omega_a = 3154$ meV, $\hbar W_b = 570$ meV, $\hbar W_a = 355$ meV, $\varepsilon_c = 3$. These values of W provide the measured values for the LT-splitting 51 and 19 meV.³ In figures 3(b)–(d) we show the zoom of the resonance region with the modes with $m = 1, 2, 3$ for the angles $\varphi = 0^\circ, 45^\circ$ and 90° . Each mode is marked with its value of m . The continuous (dot- and-dash) lines denote $\omega_B(m, \mathbf{k})$ ($\omega_A(m, \mathbf{k})$) (14), the horizontal dashed lines denote the resonance energies $\hbar\omega_a$ and $\hbar\omega_b$. The modes $\omega_A(m; \mathbf{k})$ and $\omega_B(m; \mathbf{k})$ are perpendicularly polarized and demonstrate the behavior similar to the case of a uniaxial crystal: indeed, for the angles $\varphi = 0^\circ$ and 90° the modes split into TE- and TM-polarized waves. Then for $\varphi = 0$ (figure 3(b)) the modes interacting with the a -exciton are TE-polarized, and the modes interacting with the b -exciton are TM-polarized. Correspondingly, $\omega_B(m, \mathbf{k})$ demonstrate the intercrossing at $\omega = \omega_b$, $k = \omega_b \sqrt{\varepsilon_c}/c$, and $\omega_A(m, \mathbf{k})$ form a set of modes converging to ω_a from below. For $\varphi = 90^\circ$ (figure 3(d)), in contrast, the modes interacting with the a -exciton are TM-polarized, and the modes interacting with the b -exciton are TE-polarized, and this correspondingly changes the behavior of the modes (the modes $\omega_A(m, \mathbf{k})$ demonstrate the intercrossing, and the modes $\omega_B(m, \mathbf{k})$ converge to ω_b from below). In figure 3(c) ($\varphi = 45^\circ$) the situation is intermediate, as in this case there are no purely TE- or TM-polarized modes. The modes merge to the frequencies of the excitonic resonance with the growth of m , as is typical for materials with narrow bare exciton bands (i.e. with weak spatial dispersion).

From the figures one can see that the polaritonic modes with $m = 2$ form wide (~ 40 meV) bands in the gap. We

³ The magnitudes $\hbar W$ for the model of ideal mirrors are equal to the Rabi splitting energies for the modes with $m = 1$. The values which we use (the ones deduced from the LT-splitting) exceed the Rabi splittings measured in the experiment ($\hbar\Omega_b = 340$ meV and $\hbar\Omega_a = 200$ meV) by a factor ~ 1.7 . We believe that this discrepancy between the experimental numbers originates from the fact that in the experiment the DBRs are used as mirrors, and the overlap between the electric field and the exciton is not complete. Thus we use the LT-splitting as a reference parameter, as it does not depend on the properties of the mirrors, but on the material only.

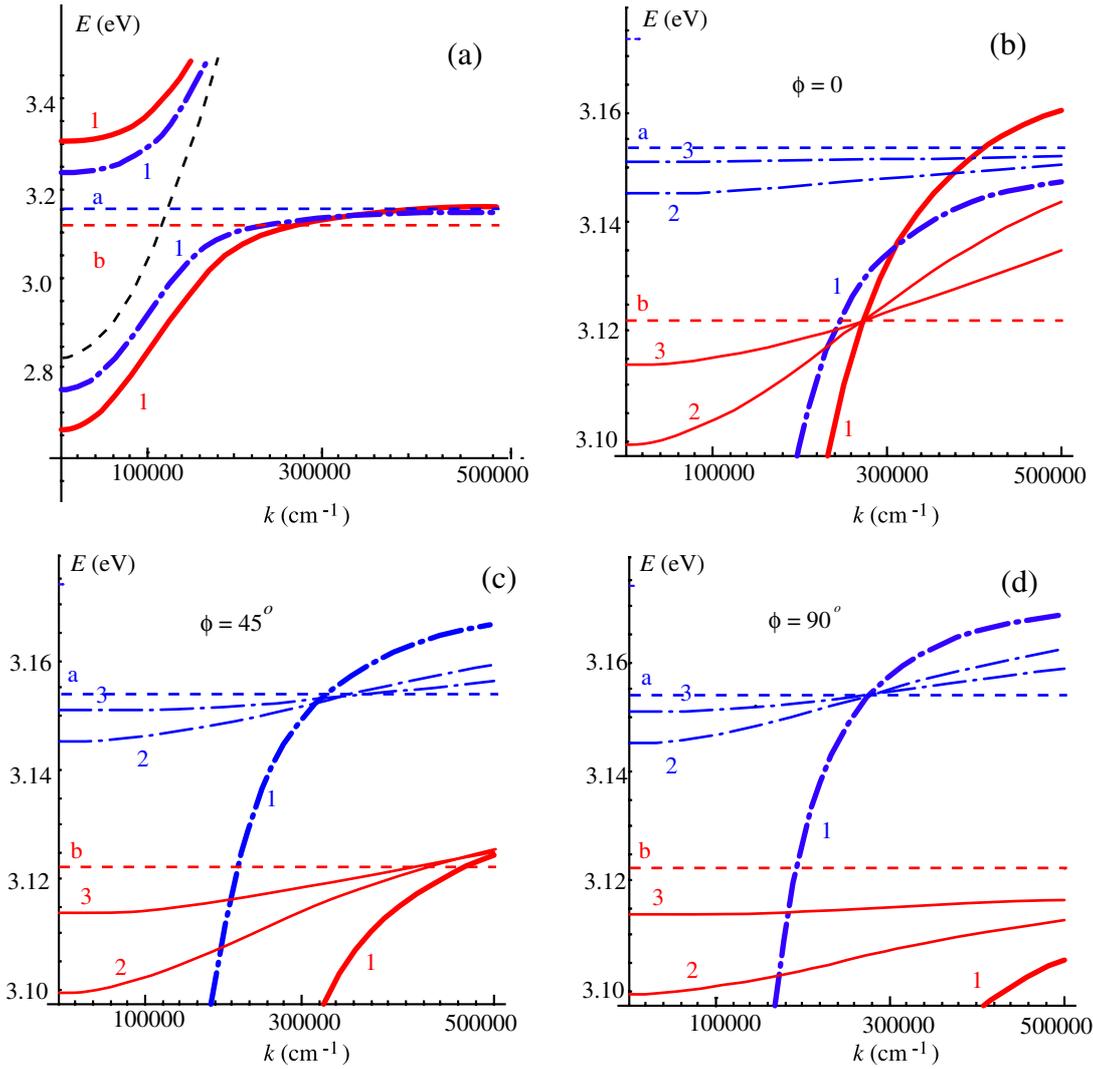


Figure 3. Dispersion of cavity polaritons in a crystal of anthracene ($\omega_T = \text{const}$, large oscillator strength of the exciton transition). *b*-exciton-like (*a*-exciton-like) modes are shown by solid (dot- and-dash) lines. (a) Conventional cavity polaritons ($m = 1$); (b)–(d) in-gap modes with $m = 2, 3$ for different angles between \mathbf{k} and the x -axis.

checked that, as expected, the account of the dependences of ω_a and ω_b on the wavevector does not influence the figures due to the largeness of the Frenkel exciton effective mass ($M_* = 5m_e$ has been taken for the check). Clearly, in this case the splitting between the in-gap polaritons and the large width of their bands is a result of a large oscillator strength of the electronic transition only (see (14)). Thus one can expect that materials with either large oscillator strength or with a strong dependence of the resonance frequency on the wavevector are more suitable for the appearance and observation of the in-gap modes.

3. Conclusions

We have discussed theoretically the dispersion of in-gap polaritons, which appear in the strong coupling regime in microcavities uniformly filled by a resonant material. These modes appear within the Rabi splitting gap (or in some cases can be resonant with the upper polariton branch) and represent

exciton-like polaritonic states with a small admixture of light (the higher m , the smaller the admixture). The modes with smaller m can be bright and have been already observed in experiments. The higher m , the smaller is the mean excitonic polarization (as m determines the number of oscillations along the z -axis). Consequently, states with higher m have a lower radiation rate.

The energy of the in-gap modes is a sum of two terms, the first is the bare exciton energy, the second is the polaritonic (retardation) correction. Both these terms can contribute to the separation between modes with different m . The first term contributes if the dependence of the exciton energy on the wavevector is strong (the separation $\sim \hbar k_m^2 / 2M_*$). The second term contributes if the oscillator strength of the excitonic transition is large (the separation $\sim W^2 / \omega_{\text{cav}}(m; k)$). Depending on the ratio between M_* and W , these two contributions may be of the same order, or one of them may dominate. In the examples considered the first term was dominant in the GaAs microcavity, and the second term was dominant in anthracene.

The in-gap modes considered are a common feature of all the microcavities exhibiting a strong coupling regime provided that the resonant material is wide enough so that an excitonic polarization with different z -symmetry can develop. As they appear as a result of quantization of the excitonic states caused by the confinement, they should be taken into account for any macroscopic width of the layer of the resonant material (i.e. also when a macroscopic layer fills the microcavity only partially). In conventional inorganic microcavities, however, the quantum well is thinner than the Wannier–Mott exciton Bohr radius. Its width is small in comparison with L and the quantization in the z -direction analogous to the one considered here does not arise. In contrast, in organic microcavities, where a resonant material with a large oscillator strength conventionally fills all the space between the mirrors, these modes should not be overlooked. As these modes are located in the middle of the gap or are in resonance with the upper polariton, they may play an important role in the energy relaxation processes.

Finally, we note that in this paper only idealized disorder-free crystals are considered. Organic crystals in reality contain a certain amount of disorder, and the amorphous structures (such as J aggregate based microcavities) are disordered by their nature. As took place in many experiments, we assumed that polaritons with $m = 1$ are in the strong coupling regime with a substantial Rabi splitting (for polaritons with $m > 1$ the discussion in terms of strong or weak coupling is not appropriate, as the interaction is non-resonant). The disorder may alter the picture presented in this paper in the following way. As the in-gap polariton modes have small group velocities (their dispersion is flat), disorder can result in the appearance of coexisting localized and delocalized states [10]. The presence

of disorder can lead also to the mixing of modes with different m : if the disorder-induced broadening of the in-gap modes exceeds the splitting between them, they cannot be resolved and can manifest themselves only as an incoherent emission from the gap. Effects related to disorder are beyond the scope of this paper and require further consideration.

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