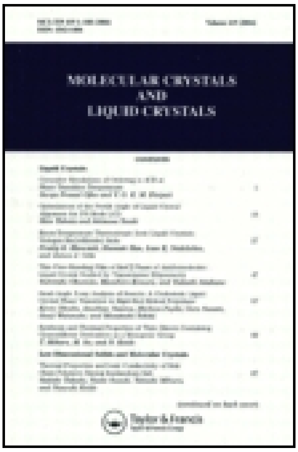

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Excitons in Organic Superlattices

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EXCITONS IN ORGANIC SUPERLATTICES

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Abstract We discuss the properties of electronic excitations in organic structures appearing in the transition from monolayers to bilayers, trilayers and so on to superlattices. In such media the possibility to govern spectra of electronic excitation of interfaces is promising. We consider the main interactions which determine these spectra and show that, since in organic media, as a rule, excitons of small radius (Frenkel and charge transfer excitons) occur, the creation of a new class of structures in which the formation of spatially separated Frenkel and charge transfer excitons can be possible. In such structures the unusual channels of photo- as well as photo-electrical transformation are of interest. In a talk we touch upon the superradiance of two-dimensional excitons and biexcitons and also the theory of optical properties of short- and long-period organic superlattices including their properties under the influence of external fields.

INTRODUCTION

The theory of excitons in unconducting molecular crystals can now be considered, apparently, as adequately formulated and able to give at least a qualitative description of experiment. What was said belongs first of all to the field of linear optics. Nonlinear optics (laser spectroscopy) makes actual some new problems from time to time. However, for the solution of these problems up to now it was not necessary to develop any new principles or conceptions.

As an example of new phenomena in molecular crystals which have not been under discussion before let us mention the kinetics of excitonic grating decay in anthracene crystals[1]. The use of the polariton picture for the region of lowest excitonic states made it possible to understand the peculiarities of this kinetics in terms of the diffusion of polaritons rather than the diffusion of excitons (see [2]) and at the same time made actual the development of a theory of four-wave mixing in which polariton zero order states, and not the excitons, shoud be incorporated in the calculation of $\chi^{(3)}$

(see [3]). We may also mention the problem of biexcitons in molecular crystals. In semiconductors one of the most important effects of optical nonlinearities is the formation of bound states of two excitons, known as biexcitons or excitonic molecules. Biexciton formation usually results in a new fluorescence line, and in a dramatic enhancement of two-photon absorption[4]. In addition, virtual biexciton states make an important contribution to nonlinear susceptibilities[5]. The important role of biexcitons in semiconductors has been confirmed by numerous theoretical and experimental studies[6]. The formation of biexcitons in molecular crystals has been discussed as well[7]. However, so far their existence has never been confirmed experimentally. The existence of such states would be important also in the context of the study of collective properties of small radius excitons. It is well-known that small radius excitons, strictly speaking, are not bosons. For example, in the case of the two-level system model for molecules they are paulions (on the collective properties of the Frenkel excitons see ref. in [7]). After V.L. Broude's death the experimental investigations of high density excitons in anthracene have been discontinued. The lack of new experimental results does not stimulate further development of the theory.

The list of unsolved or not appropriately investigated problems of exciton physics in molecular media should be continued. It is not our task to do it here, however, because in most cases these problems are not new and their discussion can be found in the literature. In our talk we discuss the spectra of organic superlattices. Structures of such type were obtained and investigated for the first time by the Forrest group[8]. In this work the molecular beam epitaxial method has been succesfully applied in growing molecular multilayers. In the paper [8] it was literally stated that: "Multiple quantum well structures consisting of alternating layers of two crystalline organic semiconductors, namely 3,4,9,10 perylenetetracarboxylic dianhydride (PTCDA) and 3,4,7,8 naphthalenetetracarboxilic dianhydride (NTCDA), have been grown by organic molecular beam deposition. The individual layer thicknesses in the multilayer samples were varied from 10 to 200 Ångstroms. X-ray diffraction and birefringence data showed that there is a strong structural ordering in all layers, as well as across large spatial distances along the sample surface. Thus, the growth was "quasi-epitaxial" even though the PTCDA and NTCDA crystal structures are incommensurate".

We believe that it was an important achievement and we will discuss below the properties of superlattices which may be obtained in this way.

FRENKEL AND CHARGE TRANSFER EXCITONS IN ORGANIC SUPERLATTICES

Note, first of all, that superlattices are systems with "condensed" interfaces, since in these artificial layered crystals the total area of interfaces is proportional to the volume. In these conditions the specific surface and quasi-two-dimentional effects must make an important contribution to the bulk crystal properties.

We begin our consideration of the properties and the role of interfaces with the boundary of anthracene crystal with vacuum. Of course, it is a particular case of boundary. However, this case has been investigated in many experiments[9] and therefore can be considered as some kind of experimental foundation of the approach we will use.

It can be considered now as well-established that 2D exciton state - the lowest electronic excitation of external monolayer of anthracene crystal - is blue shifted by 204 cm^{-1} with respect to the bottom of exciton band in the bulk. The electronic transition of the first monolayer lies between the bulk value and the isolated molecule value which is blue shifted by 2000 cm^{-1} with respect to the bulk. The electronically excited state of the surface molecular monolayer is clearly seen in emission at low temperature. The monolayer next to the surface is blue shifted by 10 cm^{-1} and the following one by 2 cm^{-1}. The nature of these blue shifts is now well understood and is related with the absence of neighbours for molecules in the external monolayer from vacuum side. Therefore, for these molecules the gas-condensed matter (G-CM) shift of electronic transition frequency is smaller than the G-CM shift in the bulk (see Fig.1; we assume that the surface corresponds to (**a**,**b**) plane of anthracene crystal). For temperatures low compared with the blue shift, the surface layer acts as an isolated monolayer and is an ideal system for investigation of two-dimensional excitons. Such excitons at week dephasing should exhibit a superradiant radiative decay[10]. This ultrafast decay of anthracene films was first observed in picosecond measurements conducted by Aaviksoo et al.[11]. Relative quantum yield measurements of the bulk and the surface emission indicate that the decay of the monolayer is purely

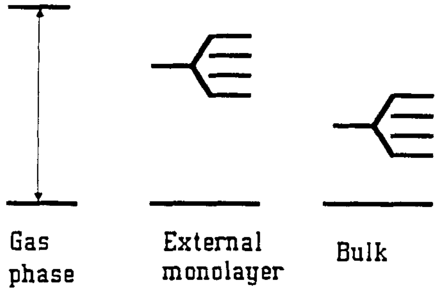

FIGURE 1 The levels on the boundaries of molecular crystals.

radiative with a very small contribution of relaxation to the bulk. The picosecond timescales observed in these experiments were a first, and a beautiful example of superradiance in two-dimensional excitons. By the way, the second example of enhanced radiative recombination of two-dimentional excitons was given very recently by Deveaud et al.[12]. In this paper radiative properties of free excitons in a single GaAs quantum well were studied under resonant excitation. Enhanced radiative recombination of the excitons was evidenced by the very short lifetime as well as by the strong intensity of the signal. In the paper [12] a radiative lifetime of 10±4 ps (in the absence of dephasing mechanisms) was deduced in quite good agreement with theory [10,13,14].

After these short remarks let us return again to the first monolayers of the anthracene crystal. As the width of the exciton band in this crystal for wave vectors directed along axis C' (i.e. along the normal to the (**a**, **b**) plane) is very small (~5 cm $^{-1}$), we can state that on the exciton's approaching the surface its energy increases (Fig. 2), interaction of exciton with surface

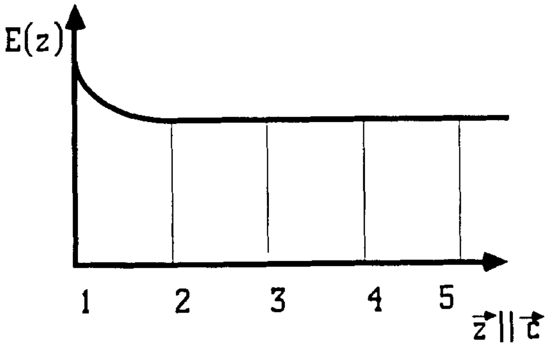

FIGURE 2 The dependence E(z) on the boundaries with vacuum.

is repulsive and we have here some type of dead layer for bulk exciton. To go ahead it is necessary to recollect how the gas-condenced matter shift can be calculated. It is known from the theory of molecular (Frenkel) excitons[1 5] that this shift appears due to the difference between the energies of interaction of the excited molecule (molecular state f) and the unexcited molecule (molecular ground state 0) with all other molecules of the crystals in ground state:

$$D^{AA}=\sum_{m} D_{nm}^{AA} \qquad (1)$$

where

$$D_{nm}^{AA}=\langle\varphi_n^{fA}\varphi_m^{0A}|V_{nm}|\varphi_n^{fA}\varphi_m^{0A}\rangle-\langle\varphi_n^{0A}\varphi_m^{0A}|V_{nm}|\varphi_n^{0A}\varphi_m^{0A}\rangle,$$

φ_n^r (r= 0A, fA) denote the wave functions of molecule A in ground (0A) and in excited (fA) state, V_{nm} is the operator of the Coulomb interaction between the molecules n and m determined by the coordinates of their electrons and nuclei $m \equiv m \equiv (m_1, m_2, m_3)$; usually the values $D_{nm}<0$ are negative for molecules with inversion symmetry (anthracene, naphtalene, etc.). For molecules n lying on the boundary with vacuum (to which corresponds, for example, space $m_3<0$) the summation over molecules m with $m_3<0$ falls out. Therefore, the respective value $D \equiv D_s^{0A}$ (below S denotes a surface, A a molecule, 0 a vacuum) can be written as

$$D^{0A}=\sum_{m_3>0} D_{nm}^{AA}\ , \qquad (2)$$

where n= (0,0,1) (here, for simplicity, we consider crystals with one molecule per unit cell), $|D_s|<|D|$ and we obtain the case represented in Fig. 1,2. In this particular case the blue shift value is equal to:

$$\Delta D \equiv D_s^{0A}-D=-\sum_{m_3\leq 0} D_{nm}^{AA}>0\ . \qquad (3)$$

Now let us consider what will occur if the crystal under consideration has boundary with another, also molecular crystal B, for example. Obviously the value of G-CM shift will change now. The shift in this case can be written as

$$D_s \equiv D_s^{BA} = \sum_{m_3>0} D_{nm}^{AA} + \sum_{m_3<0} D_{nm}^{AB} \quad , \qquad (4)$$

where

$$D_{nm}^{AB} = \langle \varphi_n^{fA} \varphi_m^{0B} | V_{nm} | \varphi_n^{fA} \varphi_m^{0B} \rangle - \langle \varphi_n^{0A} \varphi_m^{0B} | V_{nm} | \varphi_n^{0A} \varphi_m^{0B} \rangle \ . \qquad (4a)$$

Therefore, the shift of level for molecules in the first monolayer in comparison to bulk value is equal to:

$$\Delta D = D_s^{BA} - D^{AA} = \sum_{m_3<0} (D_{nm}^{AB} - D_{nm}^{AA}). \qquad (5)$$

Although each of the values D_{nm}^{AA} and D_{nm}^{AB} for the lowest electronic molecular excitations is negative, as a rule, we no longer have the possibilitity to do the definite statement with respect to the sign of the molecular level shift ΔD: this shift can be for different pairs of molecules A and B either positive or negative. Thus, if the molecules B possess in ground state relatively small static multipoles (let us denote their value conditionally by S_B) the shift ΔD should be positive, as happens for anthracene at the boundary with vacuum (by definition $S_B >> S_0$) (Fig.1, 2). If we have the opposite case and respective multipoles of type B molecules are large enough ($S_B >> S_A$) the shift ΔD can become negative. In this case instead of the situation expressed in Fig.2 we obtain attraction of excitons to the surface (Fig.3). Let us recall now that we are interested in organic superlattices and

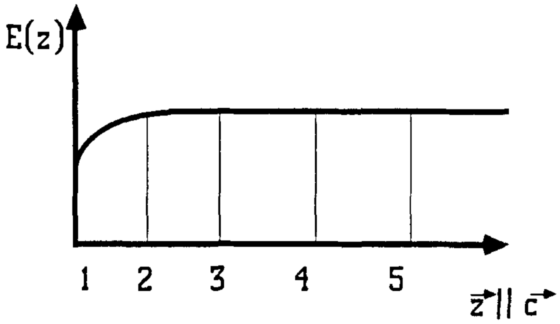

FIGURE 3 The dependence E(z) in the case $S_B > S_A$.

assume that we have under discussion the superlattice of type B A B A B ... . Then we have the case shown in Fig.4 for the exciton energy E(z) at $S_A > S_B$;

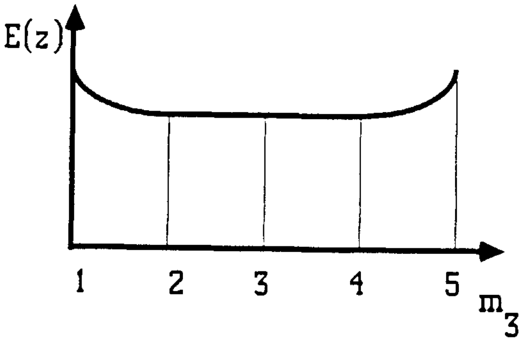

FIGURE 4 The dependence E(z) for A layer in the case $S_A > S_B$.

at $S_A < S_B$ the dependence E(z) is different (see Fig.5; for definiteness the Figs. 4 and 5 correspond to five lattice constants in A-layer).

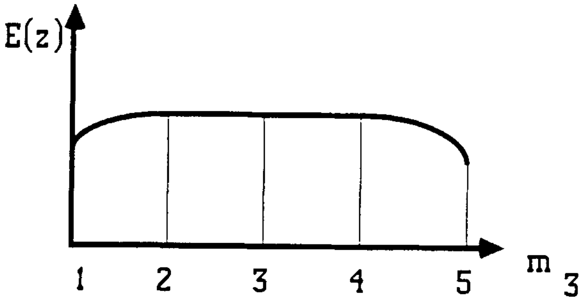

FIGURE 5 The dependence E(z) for A layer in the case $S_A > S_B$.

Let us stress an important circumstance now. The molecule and crystal of anthracene which we have used above as a well-investigated example, possess an inversion center. The dipole moment operator for such molecules can have only nondiagonal nonzero matrix elements so that the quantities D_{nm} depend only on the quadrupole moment and higher moments. Therefore, the quantities D_{nm} in this case containing only diagonal matrix elements of the operator of intermolecular interaction rapidly decrease with increasing n-m and it proves sufficient to take into account the interaction between nearest neighbours in order to calculate their contribution to the exciton energy. That is why the shift of molecular levels in comparison to the bulk value for anthracene molecules is important only for the first and probably for the second external monolayers in anthracene crystal.

For the crystals without an inversion center the long-range dipole-dipole interaction becomes very important, while the special role of external monolayers (together with the dependence of exciton spectra on the layer thickness) becomes more weakened. This interesting case needs an elaborate analysis (see also below).

Let us consider now the conditions under which the dependences of the type expressed in Fig.4, 5 have a physical sense. It is useful again here to return to the case of anthracene crystal in the vacuum-crystal contact region. The homogeneous width γ of the lowest exciton transition in anthracene crystal at low temperature is, as was mentioned, of the order of 10-20 cm^{-1}, i.e.,of the order of the width of exciton band Δ (for wave vectors k which are parallel to axis C'). Therefore, in layers of anthracene type in which the inequalities

$$|\Delta D| \gg \gamma, \Delta,$$

are satisfied, the curvature of the bottom of exciton zone like shown in Fig.4,5 can be very important and it is necessary to take it into account in the discussion of optical or electro-optical processes in organic multilayer structures. In this case we have a system with large inhomogeneous broadening and this effect can be important even in the cases where the homogeneous width is of the order of the inhomogeneous width. Clearly, in the crystals to which Fig.4 corresponds the excitons created as a result of absorption of the high energy photons ($\hbar\omega$ > E(z)) after energy relaxation should be concentrated in the region of the minimum of the function E(z), that is in the one of middle monolayers (the monolayer m_3=3 in Fig. 4). In the structures of another type to which Fig.5 corresponds the excitons should be concentrated in the interface region.

The concentration of excitations in both cases can lead, under some evident conditions, to the appearance of the inverse population of electronic states. However, we do not consider this possibility here since it is rather similar to what takes place in semiconductor heterostructures. Here we consider the role of charge transfer excitations, which can be interesting for the photoconductivity of organic multilayer systems. Let us assume, for example, that the pair of molecules A and B has an excited state with charge transfer and that the energy of this state lies below the lowest energies of electronic excitation of separated molecules A and B (that is below the lowest energies of Frenkel excitons in crystals A and B, as happens in the usual electron donor-acceptor crystals[16]). Let us assume also that in the region of A-B interface the molecules have neutral ground state. In this case in the layers where the function E(z) has the shape shown in Fig.5 the pumping of Frenkel excitons can give rise to their concentration along interfaces with the subsequent transformation into the two-dimensional charge transfer (CT) excitons.

It is well-known now that in many molecular media the CT exciton states contribute to the photoconductivity by acting as intermediates in the photogeneration of charge carriers[17]. It means that in organic superlattices which we discuss here the absorption of light in the bulk of superlattice can be transformed into photoconductivity along the boundaries of layers.

The CT exciton in electron donor-acceptor crystals with neutral ground states usually lies quite close to the lowest conduction band[16]. If we assume the same situation in the region of A-B interface, that is the 2-D CT exciton lies below and quite close to the lowest 2-D conduction band of interface, we will be able to expect the appearance of the thermally activated charge carrier production with some small activation energy. If the molecules in the region of interfaces have ionic ground state (as for the segregated stack organic solids[16]) it is possible to expect appreciable 2-D electrical conductivity. In both cases the discovery and the investigation of the above-mentioned 2-D photoconductivity as well as 2-D conductivity may be of great and independent interest. Let us note only that the scenario of the electronic energy transformation which we have traced here quite qualitatively does not mean the unique possibility for such a scenario. The field for the speculations with the molecular engineering remains naturally quite wide. In particular, it is not necessary to have the large number of layers, and in creation of multicomponent structures such variants of theirs are possible where the energy can be concentrated only in the region of one interface. Let us consider, for example, the structure B-A-C in which for static multipoles the inequalitities SB>SA>SC take place. It is clear that in this case for Frenkel excitons in layer A the exciton energy E(z) has the form expressed in Fig.6 and it confirms what has been stated.

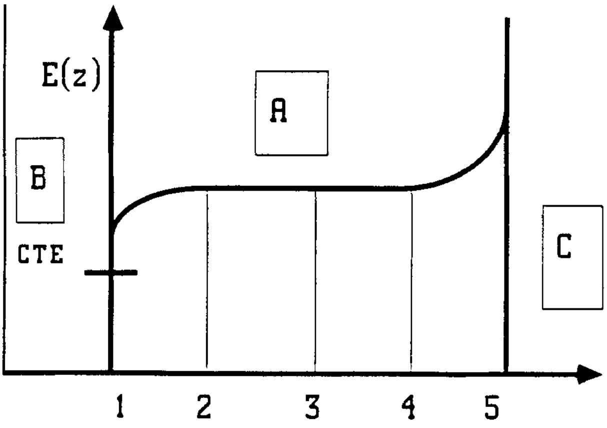

FIGURE 6 The dependence E(z) for A layer in the case $S_B > S_A > S_C$.

GAS-CONDENSED MATTER SHIFT AND DIPOLE-DIPOLE INTERACTION

Let us now consider organic multilayer systems in which molecules possess in their stationary states the static dipole moments. If in this case the dipole-dipole interaction dominates, the relations for G- CM shift take a more descriptive form. As it follows from relation (4a) the quantity D^{AB}_{nm} can be written in the following way:

$$D^{AB}_{nm}=(P^{fA}_i-P^{0A}_i)T_{ij}(n,m)P^{0B}_j,$$

where P^{fA} and P^{0A} are static dipole moments of molecule A in ground(0) and in excited(f) state, P^{0B} the static dipole moment for molecule B in ground state, Tij(nm) the tensor determining the interaction of dipoles situated in points n and m. Therefore, according to eq.(5) we obtain

$$\Delta D=\sum_{m,m_3<0} \mu^A_i(0,f)\ T_{ij}(n,m)\ \mu^B_j(0),$$

where

$$\mu^A_i(0,f)=(P^{fA}_i-P^{0A}_i)\ ,\quad \mu^B_j(0)=(P_j^{0B}-P_j^{0A})\,.$$

Thus, in this case the shift ΔD is equal to the energy of interaction of the difference dipole moment $\mu^A(0,f)$ on the site n with the network of dipoles $\mu^B(0)$ located on the lattice sites m with negative component m_3. Note again that in dependence on the directions of $\mu^A(0,f)$ and $\mu^B(0)$ the shift ΔD can be positive as well as negative. Let $\mu^A(0,f)\approx \mu^B(0) \approx 5$ Deb., lattice constant $a\approx 5$ Å, then eq. for ΔD gives an order-of-magnitude estimate $\Delta D \approx 1000\ cm^{-1}$. This very crude estimation indicates nevertheless that for molecules without inverse symmetry the shifts ΔD will be determined by dipole-dipole interaction.

THE FRENKEL-WANNIER-MOTT EXCITON COEXISTENCE

In the beginning of this talk it was already stressed that the total area of interfaces in superlattice is proportional to its volume. It means that existence of interfaces can affect the bulk properties of superlattices. Now we will be interested in their static dielectric constants. In molecular crystals this quantity is usually $\varepsilon(0)\approx 3\text{-}4$. For example, the mean experimental value in anthracene $\varepsilon = 3.23$. Even in organic semiconductors $\varepsilon(0)\approx 3$ (see [18]). Therefore, for molecular crystals it is reasonable to take into account the Wannier-Mott excitons, probably, only for high values of the quantum number n >>1, for which the radius of states becomes large in comparison with the lattice constant. But for high values of n (i.e. for energies just below the energy gap), the density of exciton states is proportional to n^3, the intensity of dipole transition is proportional to $1/n^3$, and, as a result, the exciton states are able to give only a constant value of the absorption coefficient at the ionization limit[19]. Thus, in molecular crystals the states of Wannier-Mott excitons with small n =1,2,3 do not exist. Instead of these states we have the Frenkel excitons which no longer are genetically related with the gap. The energies of these excitons reflect the positions of molecular terms and in all cases the lowest term lies significantly below the gap. However, in organic superlattices the situation is likely to be richer. Let us assume, for example, that in the interface region the molecules A and B are able to have low-lying and dipole-active electronic charge transfer excited states. Under the influence of these states the static dielectric constant can be increased and if this increasing is large enough the states of Wannier-Mott excitons with small quantum numbers n become possible. Of course, in this situation we will have two-dimensional excitons located in organic quantum wells. Let us mention, also, that the same effect can be achieved if the substance in the barriers (for example, in layers B) has high value of static dielectric function.

The electron-hole interaction in our anisotropic case in the layer A on the distances $\rho \gg L$, L is the period of superlattice, given by expression

$$V(\rho) = -e^2/\rho\sqrt{\varepsilon_{\|}\varepsilon_{\perp}},$$

where $\varepsilon_{\|} = \varepsilon_{zz}$, $\varepsilon_{\perp} = \varepsilon_{xx} = \varepsilon_{yy}$. In the paper [20] it was shown that if the contribution of interfaces in the superlattices of type A B A B A... is taken into account the dielectric constant of superlattice (here we consider the case of uniaxial crystal symmetry for superlattice) is given by expressions

$$\varepsilon_{\perp} = \frac{1}{l_1 + l_2}(\varepsilon_1 l_1 + \varepsilon_2 l_2 + 2\nu),$$

$$\varepsilon_{\|}^{-1} = \frac{1}{l_1 + l_2}\left(\frac{l_1}{\varepsilon_1} + \frac{l_2}{\varepsilon_2} + 2\mu\right),$$

where ε_1 and ε_2 are the static dielectric constants of substances in A and B layers, μ and ν are the the constants which characterize the static response of the transition region near the interfaces. It is clear that the contribution of interfaces (of course, if their polarizabilities are high enough) can be in particular substantial for the short period superlattices. Anyway, if for the static dielectric constants the realization of the condition

$$\sqrt{\varepsilon_{\|}\varepsilon_{\perp}} \gg 1,$$

can be achieved, then in organic quantum wells a few types of lowest electronic states appear. The CT exciton in the interface will be lowest, the next, probably, will be Frenkel exciton and the next - Wannier-Mott exciton with n=1 in organic quantum well. In the case when the state of Wannier-Mott exciton has energy larger in comparison with the energy of the mentioned Frenkel exciton the channel of the radiationless transition to the state of Frenkel exciton will open. It is interesting that the probability of this transition - the same as the probability of radiative transition to the ground - state is proportional to the factor

$$P \approx \frac{d^3}{a_B^2 l_1},$$

where d is the lattice constant, a_B Bohr radius, l_1 the thickness of organic layer, because in both cases in the processes of annihilation an electron and a hole have to appear on the same molecule.

ON SUPERRADIANCE OF BIEXCITONS: CAN FAST RADIATIVE DECAY COMPENSATE THE WEAKNESS OF NONLINEARITY?

In the paper [21] a new possibility for observing biexcitons in two-dimensional microstructures was pointed out. The main idea was that in two-dimensional systems (quantum wells or molecular monolayers) at low temperature a biexciton will exhibit a superradiant radiative decay, very similar to what was observed by Aaviksoo et al.[11] and by Deveaud et al.[12] for ordinary 2D excitons. This may allow the observation of fluorescence in which the entire biexciton energy is transferred to a photon with $h\omega = E_B(k)$. This channel can therefore compete with the decay to an exciton and a photon which is normally observed in semiconductors[6]. In molecular crystals fast superradiant radiative decay may compete with exciton - exciton annihilation.

In the paper [21] a case of molecular crystal with Frenkel excitons was discussed. It is interesting also to develop a similar approach for semiconductor quantum wells.

DIELECTRIC TENSOR AND INFLUENCE OF EXTERNAL FIELDS ON OPTICAL PROPERTIES OF ORGANIC SUPERLATTICES

If the period of a superlattice L is small in comparison with the light wavelength its optical properties can be described, as for usual crystals, by the phenomenological Maxwell equations with the use of some expression for the dielectric permeability tensor of the superlattice. In [20] a simple method was proposed to obtain this tensor: this method allows one to express the tensor of superlattice in terms of dielectric constants in individual layers and it is based on the use of continuity at interfaces of layers of some components of macroscopic field. This method was afterwards used efficiently to determine also the magnetic permeability tensor of some magnetic superlattices (see for a review [22]) and later in [23] to obtain dielectric tensor of the superlattice in the case when dielectric constants in individual layers are arbitrarily anisotropic. The results obtained were used to find tensors which determine the influence of external static electric and magnetic fields on optical properties of dielectric superlattices. In the paper [23] components were found of the dielectric tensor of superlattice in terms of dielectric tensors in individual layers and in terms of ratios l_i/L, where l_i is the thickness of i-th layer, $i = 1,2...\sigma$, σ is the number of layers in a unit cell of superlattice,

$$L=\sum_i l_i$$

is the superlattice period. The final expressions for these components in the general case are rather cumbersome but the reader can find these expression in [23]. The results of this paper make it possible to investigate the influence of anisotropy in individual layers on the optical properties of superlattices and in particular on the positions of excitonic resonances. In the paper [20] it was shown that the same approach can be used for calculation of nonlinear polarizabilities of superlattices in terms of nonlinear polarizabilities in individual layers.

In conclusion, let us also note that in the paper by Forrest et al. [8] the first experimental spectroscopic investigations of excitons in organic superlattices were performed. These investigations give information on a considerable dependence of excitonic transition frequencies on the layer thicknesses. It was found from the optical absorption spectra that the lowest energy PTCDA singlet exciton line shifts to the higher energy with decreasing layer thicknesses. The maximal shift was found to be equal to ca. 200 cm^{-1}. It is highly possible that the observed singlet exciton shift, as we already noted in [24], is due to the effect of G-CM shift, which we have discussed above for anthracene.

If the creation of organic superlattices similar to superlattices obtained in [8] do not will be some exotics it makes actual many interesting new problems for physics of organic materials and for quantum chemistry as well. In particular, the calculations of gas-condensed matter shifts with taking into account of the mixing of molecular configurations will be important, the theory of exciton-phonon interaction, the theory of mobility of excitons and the nonlinear optics of organic superlattices and multiple quantum wells will receive new impulse for development. Like the creation of semiconductor superlattices, quantum wells, quantum wires and quantum dots have enriched the physics of semiconductors, the creation of molecular superlattices and multiple quantum wells undoubtedly will enrich the physics and quantum chemistry of molecular compounds and can prove useful for photonic device applications.

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