

Excitons in Hybrid Organic-Inorganic Nanostructures

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In two-dimensional heterostructures made of semiconductor and organic layers, when resonance between the Wannier and Frenkel excitons is realized, the dipole-dipole interaction coupling them leads to novel striking effects. First, we discuss the pronounced nonlinear optical properties of the hybrid Frenkel–Wannier excitons appearing when the energy splitting of the excitonic spectrum is large compared to the exciton linewidths (the case of strong resonant coupling). Next, we consider the case of weak resonant coupling for which the Förster mechanism of energy transfer from an inorganic quantum well to an organic overlayer is of great interest: the electrical pumping of excitons in the semiconductor quantum well could be employed to efficiently turn on the organic material luminescence.

In the last few years, much attention was devoted to the study of organic crystalline layered structures, both experimental [1] and theoretical [2]. The substantial improvement in the technique of organic molecular beam deposition has led to a variety of good quality heterostructures based on molecular solids as well as on combinations of organic and inorganic semiconductors. The possibility of growing tailor-made systems incorporating different organic crystalline materials with even more flexibility than for multiple quantum wells based on inorganic semiconductors opens up a promising field of research from the point of view of fundamental as well as applied physics.

Such technological progress prompted us to study heterostructures with resonating Frenkel excitons (FEs) in the organic material and Wannier–Mott excitons (WEs) in the inorganic one [3]. For example, the FE energy in anthracene is 3 eV, in coronene is 2.9 eV, in PTCDA 2.2 eV, in pentacene 1.5 eV. Semiconductor quantum wells with resonating WEs can be obtained from III–V and II–VI ternary solid solutions such as GaAlAs, ZnCdSe, ZnSSe, judiciously choosing the alloy composition and well thickness.

Another concern is the width of the exciton lines. In good quality inorganic semiconductor quantum wells, the WE linewidth is of the order of 1 meV (usually limited by inhomogeneous broadening). FEs in organic materials typically have a much larger linewidth (often due to strong electron-phonon coupling); for instance, about 200 meV in thin films of PTCDA [1]. However, it is possible to choose resonating organic materials with sharp FEs, such as coronene (exciton linewidth $\simeq 4$ meV [4]) or the surface exciton of anthracene (linewidth of about 1 meV [5]). It is important to note that the dipole-dipole interaction coupling the FEs and WEs at an organic-inorganic heterojunction can be of the order of 10 meV [3,6]. Therefore, the case of strong coupling (Sect. 1), in which the exciton linewidths are smaller than the anticrossing energy splitting and hybrid excitons (HEs) exhibiting pronounced optical nonlinearities are formed [3,6], must be distinguished from the case of weak coupling (Sect. 2), in which the FEs are much broader and the dipole-dipole coupling gives rise to an irreversible energy transfer from the inorganic to the organic material [7,8].

1. Strong Resonant Coupling: Hybrid Exciton Nonlinearities

In covalent semiconductor quantum wells, optical nonlinearities dominated by phase space filling effects have already attracted much interest [9]. The density-dependent susceptibility near the excitonic resonance can be written as

$$\chi(\omega) \simeq \chi^0(\omega) \left(1 - \frac{n}{n_S}\right) \simeq \frac{F^0}{\epsilon^0 - \hbar\omega} \left(1 - \frac{n}{n_S}\right), \quad (1)$$

where χ^0 is the linear susceptibility, ϵ^0 is the resonance energy and F^0 represents the oscillator strength of the exciton, n is the 2D density of excitons and n_S — the saturation density given roughly by $n_S \approx 1/a_o^2$, a_o being the exciton radius. Indicating the light intensity with I_P , we recall that $n \propto F^0 I_P$ and F^0 is, in turn, proportional to $1/a_o^2$. Thus, for a given I_P , the ratio n/n_S is approximately independent of the exciton radius. As long as the exciton radius dependence of the oscillator strength and of the saturation density cancel out, such a figure of merit of the optical nonlinear response cannot be much improved by tailoring the character of the excitonic resonance with dimensional confinement or even by changing material class [10].

Here, we focus on a novel way of achieving a large nonlinear optical response exploiting the HEs peculiar to organic-inorganic nanostructures for which the situation is quite different. The physical system we are referring to, comprises two parallel two-dimensional layers separated by a distance of a few nanometers: the first sustains tight bound FE (the size of which is of the order of a unit cell) and the second, loosely bound WE (with radius a_o of about 10 nanometers), having energies ϵ_F^0 and ϵ_W^0 , respectively, and a center of mass momentum $\hbar\mathbf{Q}$ along the layer planes (assumed to be conserved). Near resonance ($\epsilon_F^0 \simeq \epsilon_W^0$), they mix with each other via the dipole-dipole coupling $|V_{WF}^0(\mathbf{Q})|$ [3,6]. When the dipole-dipole interaction energy is larger than the exciton linewidths, the true eigenstates of the system are HEs with wavefunctions of a mixed character and modified dispersion laws [3,6], in particular when the

FE and WE are exactly in resonance the HE eigenvalues are a split doublet and the corresponding wavefunctions are superpositions of FE and WE wavefunctions with equal weights. Since the HEs possess both the large radius of Wannier excitons and the large oscillator strength of Frenkel excitons, their saturation density n_S is still comparable to that in covalent semiconductor quantum wells, but the photogenerated density n , for a given I_P , is much higher: as a consequence, the ratio n/n_S for the 2D HE can be two orders of magnitude larger than for the usual multiple quantum wells [6].

The first order nonlinear corrections can be expressed in terms of the total 2D HE density n [6,9]: the WE blue shift $\epsilon_W^1 \simeq 0.48E_b\pi a_o^2 n$ (E_b being the WE binding energy), the WE Pauli blocking factor $B_W \simeq 1 - 0.14\pi a_o^2 n$ and the correction V_{WF}^1 to the hybridization due to the modification of the WE wavefunction $|V_{WF}^0 + V_{WF}^1|^2 \simeq (1 - 0.12\pi a_o^2 n)|V_{WF}^0|^2$. All these effects are typical for Wannier excitons having a small saturation density $n_S \approx 1/a_o^2$, but here they belong to the hybrid excitons which also have a large oscillator strength characteristic of Frenkel excitons. Using a standard microscopic approach [9], we can then write the density dependent 2D susceptibility of hybrid excitons as [6]

$$\chi_{HE}(\omega; Q) \simeq \frac{F_F^0(\epsilon_W^0 + \epsilon_W^1 - \hbar\omega)}{(\epsilon_W^0 + \epsilon_W^1 - \hbar\omega)(\epsilon_F^0 - \hbar\omega) - B_W|V_{WF}^0 + V_{WF}^1|^2}, \quad (2)$$

where only the dominant term proportional to F_F^0 has been retained. In the linear regime, n is negligible and $\epsilon_W^1 \simeq 0$, $V_{WF}^1 \simeq 0$ and $B_W \simeq 1$; the poles of the linear susceptibility are just the HE doublet eigenvalues. With increasing excitation intensity, the FEs are not much disturbed due to their large saturation density, but the WEs start bleaching and this affects the above HE susceptibility. For realistic parameters, at $Q \simeq 10^7 \text{ cm}^{-1}$ we have $|V_{WF}^0| \simeq 5 \text{ meV}$ [2] and, including phenomenological linewidths of a few meV, we obtain [2,6] for the fractional nonlinear change in absorption coefficient close to resonance $|\Delta\alpha|/\alpha \approx 10^{-11} \text{ cm}^2 n$, which for a given n is of the same order as for a covalent semiconductor quantum well. However, for a given pump intensity I_P , the 2D density of photogenerated excitons n is in our case about two orders of magnitude larger ($n \propto \chi_{HE} \propto F_F^0$), as anticipated. We wish to stress that the present effect is typical of hybrid excitons and would not be effective in the case of two coupled quantum wells of the same material.

2. Weak Resonant Coupling: Förster Energy Transfer

A large effort has recently been devoted to the study of organic light emitting diodes and lasers. Förster-like energy transfer between different dye molecules in solid solutions has already been used to achieve light amplification in optically pumped organic thin films [11]. However, optically active organic materials have poor transport

properties compared to inorganic semiconductors and the efficient electrical pumping of such devices is a challenging problem. Prompted by the rapid advances of epitaxial growth techniques for crystalline molecular materials (even on inorganic substrates) [1], we consider here a novel hybrid configuration in which both inorganic semiconductors and organic materials are present: the basic idea is to pump the optically active organic molecules via electronic energy transfer from the two-dimensional Wannier–Mott excitons of a semiconductor quantum well.

We consider a symmetric structure consisting of a semiconductor QW of thickness L_w between two barriers of thickness L_b each (L_b being a few nanometers), the whole semiconductor structure being surrounded by semi-infinite slabs of an isotropic organic material. We assume that in the frequency region considered here the semiconductor background dielectric constant ϵ_b is real (the same for the well and the barrier), and that of the organic material $\tilde{\epsilon}$ is complex (due to a broad absorption band). The irreversible Förster-like energy transfer rate due to the dipole-dipole interaction can be calculated simply from the Joule losses in the organic material [7,8]. First, we calculate the transfer rate from free excitons [7,8]. We consider two polarizations: one lying in the QW plane along \mathbf{k} (L -exciton), the other perpendicular to the QW plane (Z -exciton). In Fig. 1, we plot τ_L and τ_Z as functions of exciton center of mass momentum k for parameters representative of II-VI semiconductor QWs in a realistic structural geometry. It turns out that the lifetime does not depend drastically on the polarization and the real parts of dielectric constants. The dependence on L_w is also weak. The barrier width L_b , when grows, gives an exponential factor e^{2kL_b} . As a function of k , τ exhibits a minimum at $k_{\min} \sim 1/L_b$. Typical values of k for a thermalized exciton distribution with temperature $\sim 100 \text{ K}$ are $\sim 3 \cdot 10^6 \text{ cm}^{-1}$. We see that the corresponding lifetimes (tens of picoseconds) are much less than the exciton

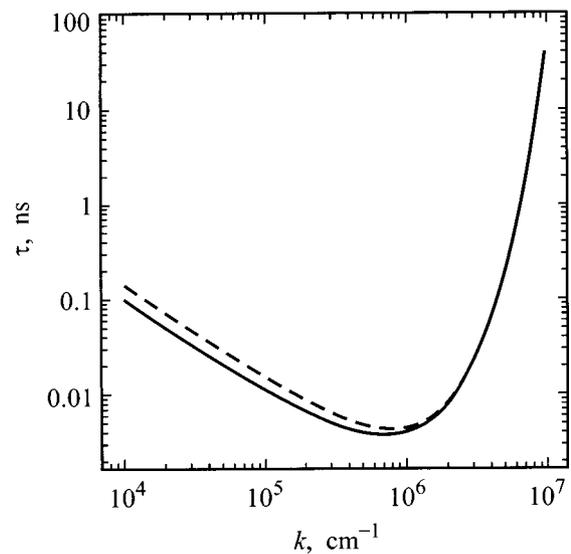


Figure 1. Free L -exciton (solid line) and Z -exciton (dashed line) lifetime τ versus the center of mass in-plane wave vector k .

recombination rate which is about 100–200 ps in II–VI semiconductor QWs. Thus the dipole-dipole transfer mechanism proves to be efficient enough to transfer a large fraction of the semiconductor excitation energy to the organic medium.

We have also studied the situation when the QW width fluctuations or the alloy disorder localize the wave function $\Phi(\mathbf{r}_{\parallel})$ of the center-of-mass exciton motion [8]. General properties of $\Phi(\mathbf{r}_{\parallel})$ are: (i) it is localized within some distance $L > L_w$, (ii) it is smooth and without nodes. Assuming the disorder to be isotropic in two dimensions, we need to consider two cases of the polarization being parallel and perpendicular to the QW plane, referred to as X and Z polarizations, respectively. It is possible to get some information about the decay rate based only on general properties of the wave function, mentioned above. We have three length scales in our problem: L_w , L_b and L . First, only $L \gg L_w$ are physically meaningful. If in addition $L \gg L_b$, we obtain $\tau \propto L$, while for a thick barrier ($L \ll L_b$) we have $\tau \propto 1/L^2$. Hence, τ has a minimum at some $L \sim L_b$. For illustrative purposes, we choose a gaussian wave function of width L and show in Fig.2 the results of the calculation (τ versus L) for realistic parameter values. We also considered the case of a quasi-thermalized plasma of free electrons and holes [8]. The dipole-dipole lifetimes obtained turn out to be as long as 300 ps (and larger) for II–VI-semiconductors.

According to our results, the kinetics of the initial free carrier population (produced, e. g., by the electrical pumping) is not significantly changed by the presence of the organic medium, since the energy transfer from free carriers turns out to be slower than the process of exciton formation (unless excitation density and temperature are very high). On the other hand, the subsequent evolution of free or localized excitons is strongly affected by the presence of the organic medium. In an isolated QW the effective lifetime of the exciton distribution may be of several hundred ps. However, excitons coupled to the organic medium a few nanometers away efficiently transfer their energy to the

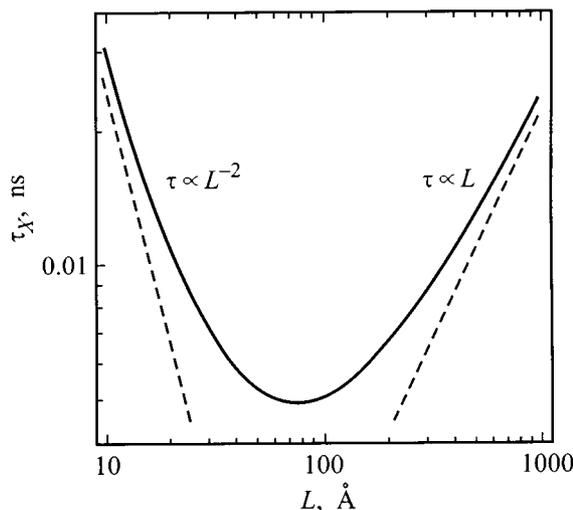


Figure 2. Localized X-exciton lifetime τ versus the localization length L (solid line) along with the limiting cases $L \ll L_b$ and $L \gg L_b$ (dashed lines).

organic molecules before they can recombine inside the QW. For quantum wells based on the II–VI semiconductors and in a realistic configuration, such transfer may occur at time scales of the order of 10 ps and be effective in activating the organic material luminescence.

To summarize, the simple physical pictures presented above may lead to new concepts for optoelectronic devices based on hybrid organic-inorganic structures, especially if embedded in a suitable microcavity [2,12]. More detailed theoretical calculations will be useful, but probably the crucial factor will be the technological progress in the synthesis of such systems. We believe that this is a very promising field of research and hope that the experimental efforts to grow and investigate these novel systems will be successful.

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References

- [1] S.R. Forrest. Chem. Rev. **97**, 1793 (1997) and references therein.
- [2] V.M. Agranovich. Molec. Cryst. Liq. Cryst. **230**, 13 (1993); Physica Scripta **T49**, 699 (1993); V.M. Agranovich, D.M. Basko, G.C. La Rocca, F. Bassani. J. Phys. Cond. Mat., in press.
- [3] V. Agranovich, R. Atanasov, F. Bassani. Solid State Commun. **92**, 295 (1994).
- [4] M. Sakurai, M. Furukawa, K. Mizuno, A. Matsui. J. Phys. Soc. Japan **61**, 445 (1992).
- [5] M. Orrit, J. Bernard, J.M. Turel, P. Kottis. J. Chem. Phys. **78**, 2847 (1983).
- [6] G.C. La Rocca, F. Bassani, V.M. Agranovich. Nuovo Cimento **D17**, 1555 (1995); G.C. La Rocca, F. Bassani, V.M. Agranovich. In: Notions and Perspectives of Nonlinear Optics, Ed. by O. Keller. (World Scientific, Singapore (1996); G.C. La Rocca. Physica Scripta **T 66**, 142 (1996).
- [7] V.M. Agranovich, G.C. La Rocca, F. Bassani. JETP Lett., **66**, 748 (1997).
- [8] D.M. Basko, G.C. La Rocca, F. Bassani, V.M. Agranovich. Submitted to European Phys. Journal B.
- [9] S. Schmitt-Rink, D.S. Chemla, D.A.B. Miller. Advances in Physics **38**, 89 (1989); H. Haug and S.W. Koch. "Quantum Theory of the Optical and Electronic Properties of Semiconductors". Ch. 16, 3rd ed. (1994), World Scientific, Singapore (1994).
- [10] B.I. Green, J. Orenstein, S. Schmitt-Rink. Science **247**, 679 (1990).
- [11] M. Berggren, A. Dodabalapur, R.E. Slusher, Z. Bao. Nature **389**, 466 (1997).
- [12] V. Agranovich, H. Benisty, C. Weisbuch. Solid. State Commun. **102**, 631 (1997); V. Agranovich, G.C. La Rocca, F. Bassani. Pure Appl. Opt. **7**, 119 (1998).