

Organic-inorganic heterostructures for nonlinear optics

V. M. Agranovich¹ and G. C. La Rocca²

¹*Institute of Spectroscopy, Russian Academy of Science,*

Troitsk, Moscow Region 142190, Russia

²*Scuola Normale Superiore and CNISM,*

Piazza dei Cavalieri, 56126 Pisa, Italy

Abstract

We consider an hybrid heterostructure made of an inorganic quantum well in close proximity with an organic material overlayer whereby the latter is used to funnel excitation energy to the former in order to exploit the optical nonlinearities of the two-dimensional Wannier excitons. The resonant optical pumping of the Frenkel excitons and their diffusion to the organic-inorganic interface can lead to an efficient indirect pumping of the inorganic quantum well turning on the corresponding nonlinearities. As organic material we consider a layer of anthracene or of tetracene. In the latter case, the singlet exciton has an energy which is close to twice the one of a triplet exciton and singlet exciton fission into two triplets can be efficient. In tetracene based hybrid heterostructures, the temperature dependence of fission opens the possibility to turn on and off the indirect pumping due to energy transfer from the organic into the inorganic subsystem. Finally, we show how a generic mechanism of dipole-dipole hybridization may lead to the formation of virtual heterodimers of organic molecules with an enhanced nonlinear optical response.

I. INTRODUCTION

The majority of modern commercial optoelectronic devices (such as LEDs, solar cells, and nonlinear-optical devices) are built on the basis of traditional inorganic semiconductors. Over the last couple of decades, however, a lot of progress has been made in producing devices based on organic electronic materials, which for many applications may become less expensive alternatives to inorganic counterparts. Various organic compounds (such as small molecules, conjugated polymers, carbon nanotubes) have been shown to be of high interest and utility in electronic applications. Advances have been reported on a variety of device types: from OLEDs¹ to organic lasers², to photovoltaic devices³. Especially impressive have been successes in organic LED development, making them a real player in a commercial arena.

The current development prospects of organic materials are however mostly limited in their scope to relatively low-performance areas. One of the reasons for this is, for instance, a low mobility of charge carriers in molecular materials. Here we use a fundamentally new direction to overcome some of the limitations of conventional material approaches using hybrid resonant organic/semiconductor nanostructures and thus creating an entirely different class of multifunctional optoelectronic materials, as it has been recognized⁴. The review paper⁵ contains the analysis of theoretical and experimental investigations of the properties of such hybrid structure considered in weak and strong coupling regimes. However, the nonlinear properties have been considered only for hybrid structures in strong coupling where it was predicted⁶, in particular, that a substantial enhancement of the resonant optical $\chi^{(3)}$ nonlinearity can be achieved in strongly coupled hybrid structures in which the eigenstates are coherent superposition of Wannier and Frenkel exciton states of the inorganic quantum well (QW) and the organic overlayer subsystem, respectively.

We focus here (following our recent papers^{7,8}) on the issue of the optical nonlinearity in hybrid structures in the weak coupling regime in which no hybrid excitons are formed, a regime which is more easily accessible experimentally. The optical nonlinearity of the inorganic QW is proportional to the concentration of excitons and e-h pairs in the well⁹. Nonlinear effects on the QW exciton resonance are observed also at room temperature and are large enough to be used for device applications¹⁰. We will argue below that an enhancement of the nonlinearity of the semiconductor QW could take place in the weak coupling

regime as well and these systems may also provide a possibility to vary the QW nonlinearity optically by changing the pumping intensity of the organic overlayer^{7,8}. The resonant absorption of light by a thin QW and the direct creation of excitons and e-h pairs in the well is small. However, the excitation density (and subsequent nonlinearity) in a hybrid structure such as the one sketched in Fig.1 can be increased due to the strong absorption of incident light by the organic overlayer (having large oscillator strength) followed by non-radiative energy transfer to the inorganic QW. Such indirect pumping of the QW can be very effective if the light from the external pumping beam will resonantly generate Frenkel excitons in the organic layer with energies significantly larger than the exciton energy in the semiconductor quantum well (i.e., at an energy at which the semiconductor already has a large absorption). The overall light absorption in the organic component of the hybrid structure can be much larger than the direct absorption by a thin QW so that the organic component plays in this case the role of a funnel of pumping radiation energy. This scheme can be viewed as complementary to that of pumping an organic medium via energy transfer from an inorganic semiconductor, proposed earlier¹¹. The process considered here can be effective if the absorption length of the organic material (i.e., the thickness required to absorb light in the organic subsystem) is not larger than the diffusion length of the Frenkel excitons, so that most of them will be able to get close to the organic-inorganic interface and to transfer their energy to the inorganic QW by the Foerster mechanism, a process which is known to be quite efficient⁶.

Following this nonradiative energy transfer and subsequent energy relaxation, the QW in the hybrid structure can reach a state with a high excitation density and thus exhibit a number of nonlinear optical effects which have attracted much attention^{9,10}. The QW Wannier exciton line which can be observed even at room temperature shifts¹² and its oscillator strength is suppressed¹³ while its linewidth broadens¹⁴ with increasing pumping until the exciton saturation density is reached and the Mott transition to an electron-hole plasma takes place¹⁵. Such optical nonlinearities would be relevant for a probe beam of light resonant with the QW exciton transition. As this probe beam has a frequency appreciably lower than the Frenkel exciton frequency in the organic overlayer, it would not be absorbed in the organic part of the hybrid structure. Variations in the pumping intensity of the organic component would produce, via nonradiative energy transfer to the inorganic quantum well, variations in the concentration of Wannier excitons in the QW, and thus optical control of

the QW nonlinearity can be achieved. For a thin QW in close proximity with the organic overlayer, this mechanism of indirect nonresonant pumping turns out to be more efficient than the one via direct optical absorption in the inorganic medium.

Following our recent papers^{7,8}, we will describe here only the main ideas and the main results of calculations demonstrating the efficiency of such indirect optical pumping. We assume first for illustrative purposes values of material parameters appropriate for a hybrid heterostructure based on II-VI inorganic semiconductors and on anthracene at room temperature. Then, we also consider as organic material a layer of tetracene. In crystalline tetracene, the singlet exciton energy is close to twice the one of a triplet exciton and singlet exciton transformation into two triplets can be efficient¹⁶. This process in tetracene is thermally activated and we investigated here how the temperature dependent exciton fission process affects the functional properties of hybrid organic-inorganic nanostructures based on tetracene. We show that the temperature dependence of fission opens a new possibility to turn on and off the indirect pumping due to energy transfer from the organic into the inorganic subsystem. Finally, we show how a generic mechanism of dipole-dipole hybridization may lead to the formation of virtual heterodimers of organic molecules with an enhanced nonlinear optical response¹⁷.

II. ANTHRACENE BASED HYBRID RESONANT HETEROSTRUCTURE

The model hybrid heterostructure we study is shown in Fig.1. The highest efficiency of the process of indirect optical pumping we consider here requires that the inorganic semiconductor material be strongly absorbing at the energy of the Frenkel exciton in the organics, and that the Frenkel exciton diffusion length L_D and the absorption coefficient α of the organic material be such that $\alpha L_D > 1$. We assume that temperature is high enough and the Frenkel excitons can be described as point dipole excitations (incoherent molecular excitons) in the diffusive regime (i.e., with a hopping time much shorter than their lifetime τ). The Foerster energy transfer also contributes to the exciton propagation and this mechanism of exciton propagation will be also taken into account below. For illustrative purposes, we make use of material parameters typical of anthracene^{18–22} for the organic overlayer and of a thin QW of II-VI semiconductors for the inorganic subsystem^{23,24}. The absorption coefficient of anthracene at the Frenkel exciton energy of about 3.1 eV is $\alpha \simeq 3.2 \cdot 10^5 \text{ cm}^{-1}$ and the

Frenkel exciton diffusion coefficient is $D = L_D^2/\tau \simeq 5 \cdot 10^3 \text{ cm}^2/\text{s}$, being $\tau \simeq 5 \text{ ns}$ and the diffusion length $L_D \simeq 500 \text{ \AA}$. The inorganic subsystem should have a band gap significantly smaller than the Frenkel exciton energy and in the calculation of the nonradiative energy transfer rate (i.e., of the effective Foerster radius R_0), it is considered as a homogeneous medium described by a complex dielectric function^{6,25}. For a Zn(Cd)Se-based quantum well (the ZnSe band gap is about 2.6 eV) at the Frenkel exciton energy the dielectric function is $\epsilon = (n + i\kappa)^2 \approx (3 + i)^2$. Under continuous pumping, the diffusion equation can be solved and the calculation of the transfer efficiency (the ratio between the number of transferred energy quanta and the total number of incident photons) leads to⁷

$$\mathcal{E} = \frac{\alpha^2 L_D^2}{\alpha^2 L_D^2 - 1} \frac{1 - e^{-\alpha L} [\cosh(L/L_D) + (\alpha L_D)^{-1} \sinh(L/L_D)]}{\cosh(L/L_D) + (z_0/L_D) \sinh(L/L_D)},$$

$$\mathcal{E} = \frac{\alpha^2 L_D^2}{\alpha^2 L_D^2 - 1} \left(\text{sech}(L/L_D) - e^{-\alpha L} [1 + (\alpha L_D)^{-1} \tanh(L/L_D)] \right),$$

where the limit $R_0^3 \gg L_D a^2$ has been taken.

where the constant z_0 is given by

$$\frac{1}{z_0} = \frac{R_0^3}{2L_D^2 a^2}.$$

Here we will discuss only an example demonstrating a strong dependence of the indirect pumping intensity on the parameters determining the diffusion process. We plot in Fig.2 the transfer efficiency as a function of the thickness of the organic layer. It is evident that the maximal efficiency of pumping takes place for an organic layer with thickness equal to the diffusion length of exciton. Of course, such effect can be expected because for more thick organic layers the number of excitons able to reach the surface of quantum well will decrease.

Finally, let us compare the obtained transfer efficiency \mathcal{E} with the efficiency $\tilde{\mathcal{E}}$ of the direct optical pumping of the semiconductor quantum well in the absence of the organics. The latter is simply given by

$$\tilde{\mathcal{E}} = 1 - e^{-\tilde{\alpha} W}, \quad (1)$$

where $\tilde{\alpha} = 2(\omega/c)\tilde{\kappa}$, $\tilde{\kappa} = \text{Im} \sqrt{\tilde{\epsilon}}$. Taking again $\tilde{\alpha}^{-1} = 300 \text{ \AA}$, for $W = 100 \text{ \AA}$ we obtain $\tilde{\mathcal{E}} \approx 0.3$, which is twice smaller than the maximal efficiency of the transfer via the organic layer, as calculated above. For a thinner quantum well, $\tilde{\mathcal{E}}$ will be even smaller, while \mathcal{E}

changes very little as long as $W > a$. The essential reason for this is the short-range nature of the Förster transfer as compared to the optical absorption length in the semiconductor. As a matter of fact, if a very thin semiconductor subsystem ($W \lesssim 50 \text{ \AA}$) could be employed on a transparent substrate, shining the pumping light from below through the substrate (see Fig.1) could lead to an even higher efficiency of indirect pumping (which may depend on the dielectric contrast of the QW/substrate interface).

III. TETRACENE BASED HYBRID RESONANT HETEROSTRUCTURE

As organic subsystem in the hybrid structure we consider now a thin layer of crystalline tetracene. The diffusion length L_D of singlet excitons in crystalline tetracene at room temperature is $L_D = 120 \pm 10 \text{ \AA}$. It increases exponentially with decreasing temperature until it approaches a constant value of $L_D = 580 \pm 50 \text{ \AA}$ below 190 K. The temperature dependence of the singlet exciton lifetime determined by exciton fission into two triplet excitations can fully account for the observed temperature dependence of the diffusion length²⁶. In fact, the exciton diffusion coefficient in crystalline tetracene is $D = L_D^2/\tau = 3.3 \cdot 10^{-3} \text{ cm}^2 \text{ s}^{-1}$ and it is with high accuracy independent of temperature. We will argue that such dependence of the diffusion length on temperature leads to the possibility to turn on or off the indirect pumping of the II-VI quantum well via energy transfer from the tetracene layer in the hybrid nanostructure of Fig.1. To undergo fission the exciton singlet in tetracene needs to obtain an additional energy of about 0.175 eV ²⁶ from the interaction with lattice vibrations and for this reason the life-time of exciton in tetracene strongly decreases with increasing temperature. This in turns leads to a strong dependence of the diffusion length on temperature. Thus, in order to obtain an efficient indirect pumping at a given temperature, it is necessary to use a tetracene layer thickness L smaller or equal to the diffusion length L_D at this temperature. Otherwise, the energy transfer from tetracene to the II-VI quantum well will be suppressed because due to fission only triplet excitons and not singlet excitons will be able to reach the barrier of the quantum well. These remarks tell us that for a given tetracene thickness L the indirect pumping via singlet excitons can be efficient only in a restricted temperature interval up to a critical temperature T_c which decreases with increasing L .

For our quantitative estimations, we made use of the analytical expression for the energy transfer efficiency \mathcal{E} given above. Here we mention only the results of our estimations in the

limit of small z_0 which is sufficiently accurate. The results obtained for the energy transfer efficiency duly taking the temperature dependence of L_D into account, are shown in Fig.3 for different thicknesses of the tetracene thin layer ($L = 200$ Å for case 1, $L = 300$ Å for case 2, $L = 400$ Å for case 3 and $L = 500$ Å case 4). Vertical lines with arrows mark the critical temperature T_c at which $L_D(T_c) = L$, beyond which the process of fission becomes so efficient that mainly triplet excitons rather than singlet excitons can diffuse to the barrier of the II-VI quantum well. The lifetime of triplets in tetracene²⁷ is 0.6 ± 0.1 μ s, their diffusion length is $L_D = 1000 \pm 100$ Å and their diffusion constant $D = (1.6 \pm 0.8) \cdot 10^{-4}$ cm² s⁻¹. Of course, while triplets do not have enough energy to contribute to the indirect pumping of the II-VI quantum well here considered, they may contribute to other processes, including charge generation. For a given tetracene thickness, a temperature change from $T < T_c$ to $T > T_c$, the time scale of which will be most likely be limited by the tiny heat capacity of the sample, can quench the indirect pumping of the quantum well because thermally activated fission of singlets occurs transforming them into triplets. As expected, the critical temperature goes down to low temperatures when the thickness of the tetracene layer is increased; in particular, $T_c = 256$ K for case 1, $T_c = 226$ K for case 2, $T_c = 206$ K for case 3, and $T_c = 184$ K for case 4. In fact, larger layer thicknesses require longer diffusion lengths for the energy transfer to be efficient and, correspondingly, lower temperatures.

IV. OPTICAL NONLINEARITIES OF HYBRID PAIRS OF ORGANIC MOLECULES

Considering here ensembles of organic molecules only and following our recent paper¹⁷, we will show that the idea of hybridization can be useful also in this case for the efficient enhancement of the nonlinear optical response. Such possibility follows from the fact that the excited electronic states of nearby molecules are in general coupled via Coulomb interaction even in the absence of wave function overlap. When two different organic molecules having a nearly resonant excited state are close enough, the dipole-dipole interaction can significantly affect their optical response. Even though they do not chemically interact, concerning their coupling to light, such molecules do not act independently, but rather as a virtual heterodimer the response of which stems from, but is different from that of each molecule alone. A simple and rather general model to estimate their resonant nonlinear susceptibilities has been developed in our recent paper¹⁷ where the details of the calculations

demonstrating the possibility to enhance the optical nonlinearity of virtual heterodimers of organic molecules can be found. Here, we explain only the main peculiarities of our consideration. To start with let's consider the situation presented in Fig. 4 where some organic molecule (molecule B) has a large transition dipole moment to the first excited state which is resonant with the lowest transition of molecule A having a small transition dipole moment. If the distance between molecules A and B is small and if the splitting $2V_{DD}$ arising due to the A-B Coulomb interaction H_{hyb} is larger than the dissipation width of the coupled states than as shown in Fig.4, the third order optical resonance nonlinearity $\chi^{(3)}$ of this virtual heterodimer can be much larger than that of molecule A alone. Analogous calculations can be done for $\chi^{(2)}$. The model of a virtual heterodimer we have described is generic and could be applied to different composite systems, non-necessarily just a pair of molecules, provided they have two, or more, subsystems having one, or more, nearly degenerate excited levels which are coupled by the Coulomb interaction, the dipole-dipole term being usually the dominant one. The strength, and the the limit, of the present model is to be independent of any specific material property or chemical trend.

V. SUMMARY

We have considered a hybrid organic-inorganic heterostructure in which the organic subsystem is funneling the optically absorbed excitation energy into the inorganic quantum well. We have developed an analytical approach to calculate the efficiency of such indirect pumping which is very accurate for most cases of practical interest, and can be easily used for any combination of materials. The relevant physical scales governing the process have been identified, both for the case of anthracene⁷ and of tetracene⁸, the latter being affected by the temperature activated singlet fission. We remark that from the experimental point of view the realization of such a hybrid organic-inorganic heterostructure working in the weak coupling regime (i. e. not requiring the formation of coherent hybrid Wannier-Frenkel excitons) should be within the reach of state of the art techniques. Finally, we also discussed how the hybridization idea can be applied to a couple of nearly resonant organic molecules to form a virtual heterodimer¹⁷ with enhanced optical nonlinearities.

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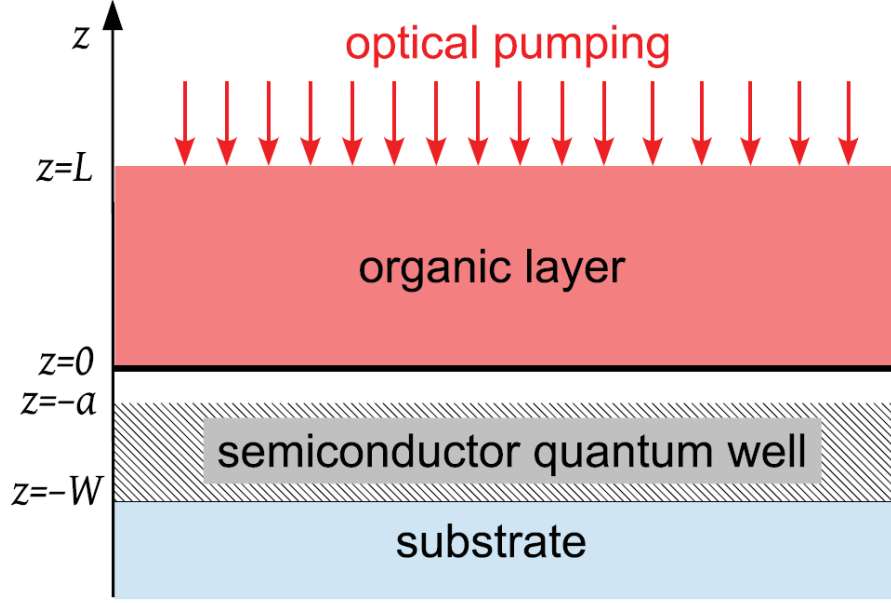


FIG. 1. (color online) Sketch of the hybrid heterostructure. In the organic overlayer (having thickness L and absorption coefficient α) Frenkel excitons are generated by optical pumping and diffuse (with diffusion length L_D) to the organic-inorganic interface, whereupon they non-radiatively transfer (with effective Förster radius R_0) to the inorganic semiconductor subsystem of thickness $W + a$ comprising a quantum well and its barriers ($a \ll W$ being the thickness of an interfacial microscopic dead layer). The indirect pumping of the quantum well is efficient provided $a \ll R_0 \sim W \ll L \sim \alpha^{-1} < L_D$ (see text for details).

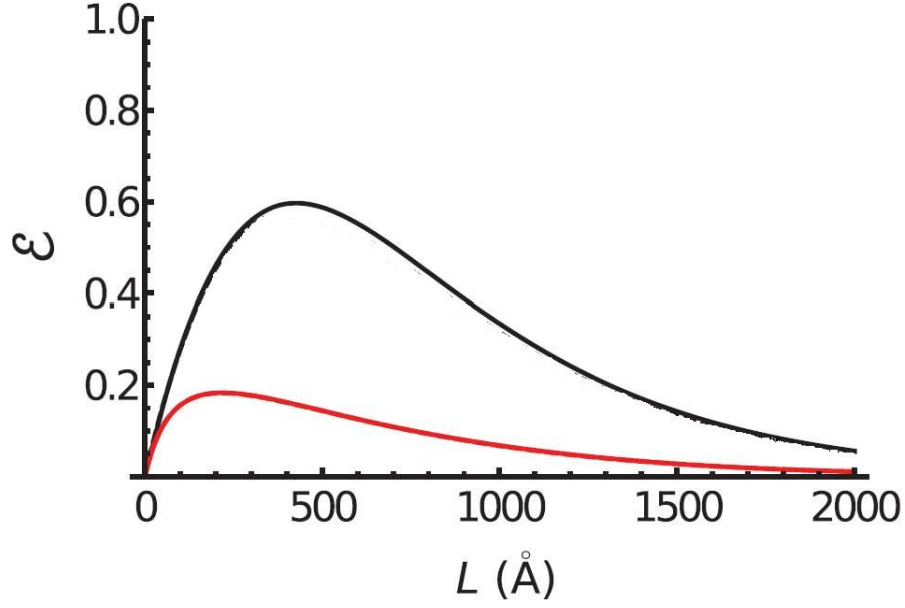


FIG. 2. (color online) Transfer efficiency \mathcal{E} as a function of the anthracene layer thickness L for two values of $R_0^3/(L_D^2 a) = 1, 0.01$ (upper and lower curves, respectively), corresponding to z_0 about 20 \AA and 2000 \AA . Other parameters are $\alpha^{-1} = 300 \text{\AA}$, $L_D = 500 \text{\AA}$, $a = 10 \text{\AA}$.

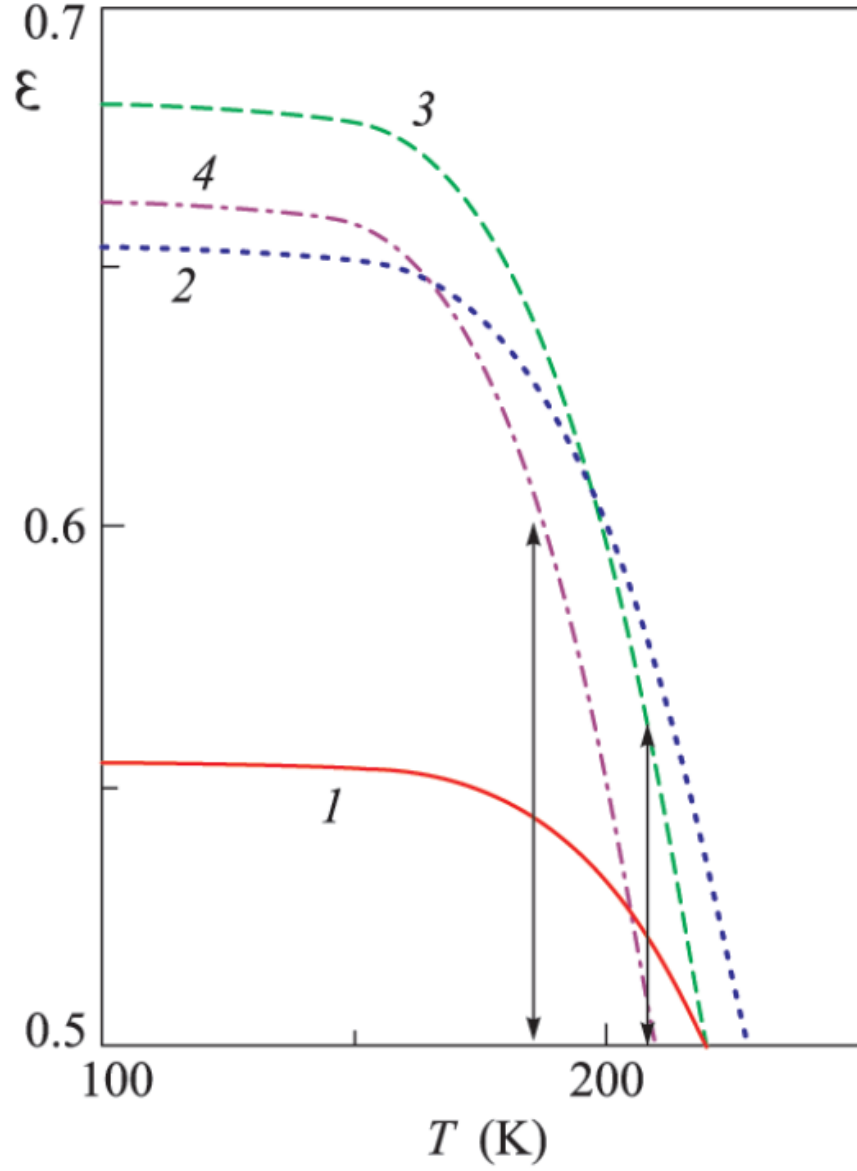


FIG. 3. (color online) Temperature dependence of energy transfer efficiency for different tetracene layer thicknesses: $L = 200$ Å for the red continuous line (case 1, $T_c = 256$ K), $L = 300$ Å for the blue dotted line (case 2, $T_c = 226$ K), $L = 400$ Å for the green dashed line (case 3, $T_c = 206$ K) and $L = 500$ Å for the purple dash-dotted line (case 4, $T_c = 184$ K).

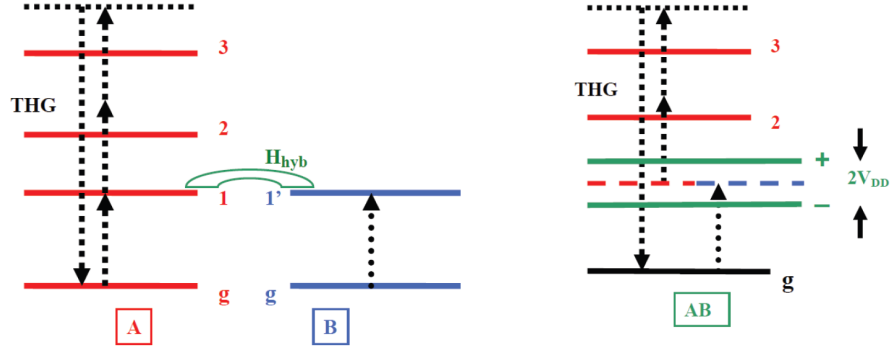


FIG. 4. Energy level scheme of a virtual heterodimer for third harmonic generation formed by two nearby molecules in which the first excited level of molecule A is nearly degenerate with the first excited level of molecule B and the two levels are coupled by the dipole-dipole interaction H_{hyb} (left panel). The first excited levels of molecule A and B give rise to a doublet of virtual dimer eigenstates: $+$ and $-$, split by $2V_{DD}$ (right panel). The third harmonic generation process (THG), nearly resonant with this doublet, also involves non resonantly two higher excited levels of molecule A .