

"Plasmonic" properties of organic materials induced by light: bistability, surface polaritons and switching waves

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Metallic inclusions in metamaterials and plasmonic systems are sources of strong absorption loss. Recently Noginov *et al.* and Gentile *et al.* demonstrated that purely organic materials characterized by low losses with negative dielectric permittivities can be easily fabricated [1,2]. And even the dramatic laser-induced change of the dielectric permittivity of organic dyes may be realized [3,4] that can enable us to control their "plasmonic" properties. The experiments with strong laser pulses [3] challenge theory. Here we develop a theory of non-steady-state organic "plasmonics" with strong laser pulse excitation. Our consideration is based on the model of the interaction of strong shaped laser pulse with organic molecules [5] extended to the dipole-dipole intermolecular interactions in the condensed matter [4]. We show that such a generalization can describe both a red shift of the resonance frequency of isolated molecules, according to the Clausius-Mossotti-Lorentz-Lorentz (CMLL) mechanism, and the wide variations of their spectra related to the aggregation of molecules into J- or H-aggregates. In particular case of weak radiation we recover the coherent exciton scattering (CES) approximation [6]. The latter is well suited to describe absorption spectra of both J- and H-aggregates using their monomer spectra and the intermolecular interaction strength that is a fitting parameter. Among other things our more general theory improves the CES results. Furthermore, the CES approximation may be used not only for linear absorption, but also for nonlinear light-matter interaction in the case of fast vibrational relaxation meaning that the equilibrium distributions into the electronic states have had time to be set during changing the pulse parameters. By this means our theory contains experimentally measured quantities (monomer spectra and the intermolecular interaction strength) that makes it closely related to experiment. Equations for populations in our theory are nonlinear ones and can demonstrate a bistable behavior. The bistability response of the electron-vibrational model of organic materials in the condensed phase due to the CMLL mechanism has been demonstrated [4]. In this case the bistable behavior of populations arises from the dependence of the resonance frequency of the molecules in dense medium on excited molecules number. The bistability response is also favoured by the aggregation of molecules. Since experiments on bistability should be done with CW pumping or pulse pumping when the distance between pulses is smaller than the excited state lifetime, the light intensity ought to be smaller than that in usual pulse experiments with thin films of dyes [3] (as to CW pumping, the damage threshold should be much smaller than 1 MW/cm^2 [7]). The resolution of the problem may be achieved using 3-electronic states system with the long-living triplet state T_1 near (but below) the excited singlet state S_1 , and fast intersystem crossing $S_1 \rightarrow T_1$. The rose bengal and other molecules are examples. In such a case one can achieve strong depletion of the ground state S_0 using intensities much smaller than 1 MW/cm^2 . We have checked that the bistable behavior persists for the 3-electronic states system. In addition, rose bengal is characterized by gigantic third order susceptibility $\chi^{(3)} \sim 10^{-3}$ esu. Furthermore, the intermolecular interactions give rise to the excitation transfer along the organic thin film as well. If the film transverse size exceeds the characteristic diffusion length, transverse phenomena such as switching waves and spatial hysteresis, known in optical bistability [8], should take place. We present the alternating-sign dependence of the switching wave velocity on pump intensity and the conditions for the spatial hysteresis realization. This gives new important information on intermolecular interactions and can form the basis of developing nano-sized schemes of molecular mass storage. In addition, the switching waves enable us to observe the bistability of the surface polaritons.

References

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