Non-steady-state organic plasmonics and its application to optical control of Coulomb blocking in nanojunctions

Guangqi Li[a], and Boris D. Fainberg[b,c],

[a]Northwestern University, Department of Chemistry, Evanston IL 60208, USA
[b]Holon Institute of Technology, 52 Golomb street, Holon 5810201, Israel
[c]Tel Aviv University, School of Chemistry, Tel Aviv 69978, Israel

ABSTRACT

Purely organic materials with near-zero dielectric permittivity can be easily fabricated. Here we develop a theory of non-steady-state organic plasmonics with strong short laser pulses that enable us to obtain near-zero dielectric permittivity during a short time. We have proposed to use non-steady-state organic plasmonics for the enhancement of intersite dipolar energy-transfer interaction in the quantum dot wire that influences on electron transport through nanojunctions. Such interactions can compensate Coulomb repulsions for particular conditions. We propose the exciton control of Coulomb blocking in the quantum dot wire based on the non-steady-state near-zero dielectric permittivity of the organic host medium.

Keywords: Nanojunctions, Organic plasmonics, Exciton effects, Coulomb blocking

1. INTRODUCTION

Metallic inclusions in metamaterials are sources of strong absorption loss. This hinders many applications of metamaterials and plasmonics and motivates to search for efficient solutions to the loss problem. In this relation the question arises whether metal-free metamaterials and plasmonic systems, which do not suffer from excessive damping loss, can be realized in the visible range? With no doubts, inexpensive materials with such advanced properties can impact whole technological fields of nanoplasmonics and metamaterials.

Recently Noginov et al. demonstrated that purely organic materials characterized by low losses with negative, near-zero, and smaller than unity dielectric permittivities can be easily fabricated.[1] And even non-steady-state organic plasmonics with strong laser pulses may be realized[2] that can enable us to obtain near-zero dielectric permittivity during a short time only.

Approach[1] was explained in simple terms of the Lorentz model for linear spectra of dielectric permittivities of thin film dyes. However, the experiments with strong laser pulses[2] challenge theory. The point is that the Lorentz model based on a mean-field theory is described by essentially nonlinear equations for strong laser excitation. Their general solution is not a simple problem. In addition, such nonlinear equations can predict multi-stability, bifurcations etc.

Here we develop a theory of non-steady-state organic plasmonics with strong short laser pulse excitation. Our consideration is based on the model of the interaction of strong (phase modulated) laser pulse with organic molecules, Ref.,[3] extended to the dipole-dipole intermolecular interactions in the condensed matter.[4,5] We also propose the exciton control of Coulomb blocking[6] in the quantum dot wire based on the non-steady-state near-zero dielectric permittivity of the organic host medium using chirped laser pulses.

Send correspondence to B.D.F.: E-mail: fainberg@hit.ac.il

Metamaterials: Fundamentals and Applications 2014, edited by Nader Engheta, Mikhail A. Noginov, Nikolay I. Zheludev,
Proc. of SPIE Vol. 9160, 91601A · © 2014 SPIE · CCC code: 0277-786X/14/$18 · doi: 10.1117/12.2059751

2. MODEL AND BASIC EQUATIONS

In this section we shall extend our picture of "moving" potentials of Ref.[3] to a condensed matter. In this picture we considered a molecule with two electronic states $n = 1$ and 2 in a solvent described by the Hamiltonian

$$H_0 = \sum_{n=1}^{2} |n\rangle \left[E_n + W_n(\mathbf{Q})\right] \langle n| \tag{1}$$

where $E_2 > E_1, E_n$ is the energy of state $n, W_n(\mathbf{Q})$ is the adiabatic Hamiltonian of reservoir R (the vibrational subsystems of a molecule and a solvent interacting with the two-level electron system under consideration in state n). The molecule is affected by a (phase modulated) pulse $\mathbf{E}(t)$

$$\mathbf{E}(t) = \frac{1}{2}\mathbf{e}\mathcal{E}(t)\exp(-i\omega t + i\varphi(t)) + \text{c.c.} \tag{2}$$

the frequency of which is close to that of the transition $1 \to 2$. Here $\mathcal{E}(t)$ and $\varphi(t)$ describe the change of the pulse amplitude and phase in time, $\mathbf{e}$ is unit polarization vectors, and the instantaneous pulse frequency is $\omega(t) = \omega - d\varphi(t)/dt$.

One can describe the influence of the vibrational subsystems of a molecule and a solvent on the electronic transition within the range of definite vibronic transition related to a high frequency optically active (OA) vibration as a modulation of this transition by low frequency (LF) OA vibrations $\{\omega_s\}$.[7–10] In accordance with the Franck-Condon principle, an optical electronic transition takes place at a fixed nuclear configuration. Therefore, the highest probability of optical transition is near the intersection Q_0 of "photonic replication" and the corresponding term and rapidly decreases as $|Q - Q_0|$ increases. The quantity $u_1(\mathbf{Q}) = W_2(\mathbf{Q}) - W_1(\mathbf{Q}) - \langle W_2(\mathbf{Q}) - W_1(\mathbf{Q})\rangle_1$ is the disturbance of nuclear motion under electronic transition where $\langle\rangle_n$ denotes the trace operation over the reservoir variables in the electronic state n. Electronic transition relaxation stimulated by LFOA vibrations is described by the correlation function $K_1(t) = \langle u_1(0)u_1(t)\rangle_1$ of the corresponding vibrational disturbance with characteristic attenuation time τ_s.[11–20]

The analytic solution of the problem under consideration has been obtained due to the presence of a small parameter. For broad vibronic spectra satisfying the "slow modulation" limit, we have $\sigma_{2s}\tau_s^2 \gg 1$ where $\sigma_{2s} = K_1(0)\hbar^{-2}$ is the LFOA vibration contribution to a second central moment of an absorption spectrum. According to Refs.,[19, 20] the following times are characteristic for the time evolution of the system under consideration: $\sigma_{2s}^{-1/2} < T' << \tau_s$, where $\sigma_{2s}^{-1/2}$ and $T' = (\tau_s/\sigma_{2s})^{1/3}$ are the times of reversible and irreversible dephasing of the electronic transition, respectively. The characteristic frequency range of changing the optical transition probability can be evaluated as the inverse T', i.e. $(T')^{-1}$. Thus, one can consider T' as a time of the optical electronic transition. Therefore, the inequality $\tau_s \gg T'$ implies that the optical transition is instantaneous. Thus, the condition

$$T'/\tau_s << 1 \tag{3}$$

plays the role of a small parameter. This made it possible to describe vibrationally non-equilibrium populations in electronic states 1 and 2 by balance operator equations for the intense pulse excitation (pulse duration $t_p > T'$). If the correlation function is exponential: $K_1(t)/K_1(0) \equiv S(t) = \exp(-|t|/\tau_s)$, the balance operator equations transform into diffusional equations. Such a procedure has enabled us to solve the problem for strong pulses even with phase modulation.[3, 21, 22]

In Ref.[3] we have obtained the following equations describing vibrationally non-equilibrium populations in electronic states $j = 1, 2$ for the intense chirped pulse excitation:

$$\frac{\partial}{\partial t}\rho_{jj}(\alpha, t) = (-1)^j \hbar^{-2} (\pi/2)\, \delta(\omega_{21} - \omega(t) - \alpha)\, |\mathbf{D}_{21}\vec{\mathcal{E}}(t)|^2 \Delta'(\alpha, t) + L_{jj}\rho_{jj}(\alpha, t) \tag{4}$$

where $\Delta'(\alpha, t) = \rho_{11}(\alpha, t) - \rho_{22}(\alpha, t)$. Here ρ_{jj} are the diagonal elements of the density matrix; $\alpha = -u_1/\hbar$, ω_{21} is the frequency of Franck-Condon transition $1 \to 2$, and the operator L_{jj} describes the diffusion with respect to the coordinate α in the corresponding effective parabolic potential $U_j(\alpha)$

$$L_{jj} = \tau_s^{-1}\left[1 + (\alpha - \delta_{j2}\omega_{st})\frac{\partial}{\partial(\alpha - \delta_{j2}\omega_{st})} + \sigma_{2s}\frac{\partial^2}{\partial(\alpha - \delta_{j2}\omega_{st})^2}\right], \tag{5}$$

δ_{ij} is the Kronecker delta, ω_{st} is the Stokes shift of the equilibrium absorption and luminescence spectra. The partial density matrix of the system $\rho_{jj}(\alpha, t)$ describes the system distribution in states 1 and 2 with a given value of α at time t. The complete density matrix averaged over the stochastic process which modulates the system energy levels, is obtained by integration of $\rho_{jj}(\alpha, t)$ over α:

$$\langle\rho\rangle_{jj}(t) = \int \rho_{jj}(\alpha, t)\, d\alpha \tag{6}$$

where quantities $\langle\rho\rangle_{jj}(t)$ are nothing more nor less than the normalized populations of the corresponding electronic states: $\langle\rho\rangle_{jj}(t) \equiv n_j$, $n_1 + n_2 = 1$.

2.1 Generalization to dense collection of molecules

Consider a dense collection of molecules, with densities such that there are many molecules within a cubic molecular resonance wavelength, with two electronic states with energies $E_1 < E_2$.

The interaction of the dense collection of such systems with electromagnetic fields can be written as

$$\hat{H}_{\text{int}} = -\sum_n \hat{\mathbf{P}}_n \cdot \mathbf{E}_{l,n} \tag{7}$$

where $\mathbf{E}_{l,n}$ is the electric field at the location of the n-th molecule (local electric field), and $\hat{\mathbf{P}}_n$ is its optical polarization operator. The local (microscopic) field is related to the Maxwell (macroscopic) field $\mathbf{E}(\mathbf{r}, t)$, Eq.(2), by[4, 15]

$$\mathbf{E}_{l,n} = \mathbf{E}(t) + \frac{4\pi}{3}\sum_{m\neq n}\mathbf{P}_m \tag{8}$$

where $\mathbf{P}_m$ denotes the expectation value of $\hat{\mathbf{P}}_m$. The second term on the right-hand side of Eq.(8) represents the electrostatic longitudinal field created by all other particles m ($\neq n$), i.e., the instantaneous dipole-dipole interactions between the molecules.

Let us introduce an excitonic operator $\hat{A}_{n,12} \equiv |n1\rangle\langle n2|$ where $|nk\rangle$ denotes the k state of molecule n.[5] Then the optical polarization operator of the n-th molecule is given by

$$\hat{\mathbf{P}}_n = \mathbf{D}_{n,12}\hat{A}^+_{n,12} + \text{H.c.} \tag{9}$$

where $\mathbf{D}_{n,kk'}$ is the transition dipole moment connecting states k and k' of molecule n, and H.c. denotes Hermitian conjugate. We also introduce operators $\hat{n}_{mk} = |mk\rangle\langle mk|$ describing the population of states $|mk\rangle$. Then the Hamiltonian of the dense collection of two-state systems under consideration can be written as

$$\hat{H} = \hat{H}_0' + \hat{H}_{int} \tag{10}$$

where

$$\hat{H}_0' = \sum_m \sum_{k=1,2} E_{mk}\hat{n}_{mk}, \tag{11}$$

E_{mk} is the energy of state k of a molecule m.

Using the Heisenberg equations of motion one obtains the equation for the expectation value of any operator $\hat{F}$

$$\frac{d}{dt}\langle\hat{F}\rangle = \frac{i}{\hbar}\langle[\hat{H}_0' + \hat{H}_{int}, \hat{F}]\rangle \equiv \frac{i}{\hbar}\text{Tr}([\hat{H}_0' + \hat{H}_{int}, \hat{F}]\rho) \tag{12}$$

where ρ is the density matrix. Straightforward operator algebra manipulations, using commutation relations, yield equations for $n_{mk} \equiv \langle \hat{n}_{mk} \rangle$ and $A_{m,kk'} \equiv \langle \hat{A}_{m,kk'} \rangle$ in the rotating wave approximation (RWA). In the derivation of these equations we kept only single-particle variables, using a factorization into population variables n_{mk} and polarizations $A_{m,kk'}$ in accordance with the local field approximation.[15] Then switching to the system that rotates with instantaneous frequency,

$$a_{m,12} = A_{m,12} \exp[i\omega t - i\varphi(t)], \tag{13}$$

we obtain equations for the quantities that vary slowly with time during the period of a light wave. Furthermore, considering a homogeneous excitation of an assembly of identical molecules ($\mathbf{D}_{n,kk'} = \mathbf{D}_{kk'}$, $E_{mk} = E_k$, $n_{mk} = n_k$, $a_{m,kk'} = a_{kk'}$), we get the extension of Eq.(4) to a condensed matter:

$$\frac{\partial}{\partial t}\rho_{jj}(\alpha,t) = (-1)^j \frac{\pi}{2\hbar^2}\delta\{\omega_{21} - p_{12}[n_1(t) - n_2(t)] - \omega(t) - \alpha\}\left(\frac{\varepsilon_b + 2}{3}\right)^2 |\mathbf{D}_{21}\vec{\mathcal{E}}(t)|^2 \Delta'(\alpha,t) + L_{jj}\rho_{jj}(\alpha,t) \tag{14}$$

where ε_b is the "bulk" relative permittivity (which can be due distant high-frequency resonances of the same absorbing molecules or a host medium),

$$p_{12} = \frac{4\pi}{3\hbar}|D_{12}|^2 N \tag{15}$$

is the strength of the near dipole-dipole (DD) interaction,[4] N is the density of molecules.

Knowing $\rho_{jj}(\alpha,t)$, one can calculate the susceptibility $\chi(\Omega,t)$[3] that enables us to obtain the dielectric function ε due to relation $\varepsilon(\Omega,t) = 1 + 4\pi\chi(\Omega,t)$:

$$\begin{aligned}\varepsilon(\Omega,t) = 1 + ip_{12}\left(\frac{\varepsilon_b+2}{3}\right)\{&\sqrt{\frac{\pi}{2\sigma_{2s}}}w[\frac{\Omega - (\omega_{21} - p_{12}(n_1(t) - n_2(t)))}{\sqrt{2\sigma_{2s}}}] - \\ &- \pi\sigma_a\left(\frac{\varepsilon_b+2}{3}\right)^2 \int_0^t dt'\Delta'(\omega_{21} - p_{12}(n_1(t') - n_2(t')) - \omega(t'), t') \\ &\times \tilde{J}(t')\sum_{j=1}^{2}\sqrt{\frac{\sigma_{2s}}{\sigma(t-t')}}w[\frac{\Omega + p_{12}(n_1(t) - n_2(t)) - \omega_j(t,t')}{\sqrt{2\sigma(t-t')}}]\}\end{aligned} \tag{16}$$

where $\tilde{J}(t)$ is the power density of the exciting radiation, $\sigma(t-t') = \sigma_{2s}\left[1 - S^2(t-t')\right]$,

$$\omega_j(t,t') = \omega_{21} - \theta_j(t,t') = \omega_{21} - \delta_{j2}\omega_{st} + [\omega(t') - \omega_{21} + p_{12}(n_1(t') - n_2(t')) + \delta_{j2}\omega_{st}]S(t-t') \tag{17}$$

are the first moments of the transient absorption ($j = 1$) and the emission ($j = 2$) spectra, $\omega_{st} = \hbar\sigma_{2s}/(k_B T)$ is the Stokes shift of the equilibrium absorption and luminescence spectra, and

$$w(z) = \exp(-z^2)[1 + i\frac{2}{\sqrt{\pi}}\int_0^z \exp(y^2)dy]$$

is the probability integral of a complex argument.[23] It is worthy to note that magnitude $\varepsilon(\Omega,t)$ does make sense, since it changes in time slowly with respect to dephasing. In other words, $\varepsilon(\Omega,t)$ changes in time slowly with respect to the reciprocal characteristic frequency domain of changing $\varepsilon(\Omega)$.

2.2 Fast vibrational relaxation

Let us consider the particular case of fast vibrational relaxation when one can put the correlation function $S(t-t')$ equal to zero. Physically it means that the equilibrium distributions into the electronic states have had time to be set during changing the pulse parameters. Using Eqs.(6) and (14), one can obtain the equations for the populations of electronic states $n_{1,2}$ in the case under consideration, which represent extending Eq.(25) of Ref.[3] to the interacting medium

$$\begin{aligned}\frac{dn_{1,2}}{dt} &= \pm\sigma_a\left(\frac{\varepsilon_b+2}{3}\right)^2\exp\{-\frac{\left[\omega_{21}-p_{12}(n_1-n_2)-\omega\left(t\right)-\omega_{st}\right]^2}{2\sigma_{2s}}\}\tilde{J}(t)\{n_2-\\ &\quad -n_1\exp\left[\hbar\beta\left(\left(\omega\left(t\right)+p_{12}(n_1-n_2)-\omega_{21}\right)+\frac{\omega_{st}}{2}\right)\right]\}\pm\frac{n_2}{T_1}\end{aligned} \tag{18}$$

where $\beta = 1/k_BT$, $n_1 + n_2 = 1$, σ_a is the cross section at the maximum of the absorption band, and we added term "$\pm n_2/T_1$" taking the lifetime T_1 of the excited state into account.

In case of fast vibrational relaxation, Eq.(16) becomes

$$\begin{aligned}\varepsilon(\Omega,t) = 1+p_{12}\left(\frac{\varepsilon_b+2}{3}\right)\sqrt{\frac{\pi}{2\sigma_{2s}}}\{w[\frac{\Omega-\omega_{21}+p_{12}(n_1(t)-n_2(t))}{\sqrt{2\sigma_{2s}}}]n_1\left(t\right)-\\ -n_2\left(t\right)w[\frac{\Omega-\omega_{21}+p_{12}(n_1(t)-n_2(t))+\omega_{st}}{\sqrt{2\sigma_{2s}}}]\}\end{aligned} \tag{19}$$

3. EXCITATION BY CHIRPED PULSES COMPENSATING "LOCAL FIELD" DETUNING

Eqs. (14) and (18) for populations are nonlinear equations where the transition frequencies are the functions of the electronic states populations. So, their solution in general case is not a simple problem. However, one can use pulses that are suitably chirped (time-dependent carrier frequency) to compensate for a change of frequency of the optical transition in time induced by the pulses themselves. This idea was proposed in studies of a two-state system in relation to Rabi oscillations in inter-subband transitions in quantum wells[24] and for obtaining efficient stimulated Raman adiabatic passage (STIRAP) in molecules in a dense medium.[5]

Let us assume that we use suitably chirped pulses compensating the "local field" detuning $p_{12}(n_1 - n_2)$ that enables us to keep the value of $\omega_{21} - p_{12}[n_1\left(t\right) - n_2\left(t\right)] - \omega\left(t\right)$ as a constant

$$\omega_{21} - p_{12}[n_1\left(t\right) - n_2\left(t\right)] - \omega\left(t\right) \equiv \Delta\omega = const \tag{20}$$

In that case one can obtain an integral equation

$$\Delta\left(t\right) = 1-\sigma_a\left(\frac{\varepsilon_b+2}{3}\right)^2\int_0^t dt'\tilde{J}(t')\Delta\left(t'\right)\left[1-S^2\left(t-t'\right)\right]^{-1/2}\sum_{j=1}^{2}\exp[-\frac{\left(\Delta\omega-\delta_{j2}\omega_{st}\right)^2}{2\sigma_{2s}}\frac{1-S\left(t-t'\right)}{1+S\left(t-t'\right)}] \tag{21}$$

for the dimensionless non-equilibrium population difference $\Delta\left(t\right) \equiv \Delta'\left(\Delta\omega, t\right)/\Delta'^{(0)}\left(\Delta\omega\right)$, the effective methods of the solution of which were developed in Refs.[3, 22]

For fast vibrational relaxation, using Eqs.(18) and (20), we get

$$\frac{dn_{1,2}}{dt} = \pm\sigma_a\left(\frac{\varepsilon_b+2}{3}\right)^2\tilde{J}(t)\exp(-\frac{\Delta\omega^2}{2\sigma_{2s}})\{n_2\exp[-\frac{\hbar\beta}{2}(\omega_{st}-2\Delta\omega)]-n_1\}\pm\frac{n_2}{T_1} \tag{22}$$

3.1 Near-zero dielectric function of dense collection of molecules excited with laser pulse

In this section we shall use Eqs.(19) and (22) to demonstrate obtaining near-zero dielectric function in non-steady-state regime. We shall consider a dense collection of molecules ($N \sim 10^{21} cm^{-31}$) with parameters close to those of molecule LD690:[3] $\sqrt{\sigma_{2s}} = 546cm^{-1}$, $D_{12} \sim 10^{-17}$ CGSE that gives $\omega_{st} = 1420cm^{-1}$, $p_{12} = 3.972 \times 10^{14}\ rad/s$. We shall put $\varepsilon_b = 1^1$ and $\Delta\omega = -420cm^{-1}$. Figs.1, 2 and 3 show the population of excited electronic state n_2 and the real $\varepsilon'(\Omega, t)$ and imaginary $\varepsilon''(\Omega, t)$ parts of $\varepsilon(\Omega, t)$ for $\Omega - \omega_{21} = -2.0405\sqrt{2\sigma_{2s}}$ during the action of a rectangular light pulse of power density $\tilde{J}$ that begins at $t = 0$.

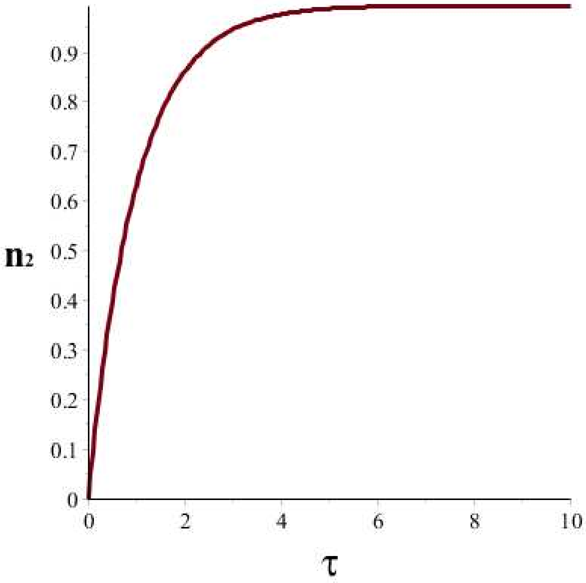

Figure 1. Population of excited state as a function of time.

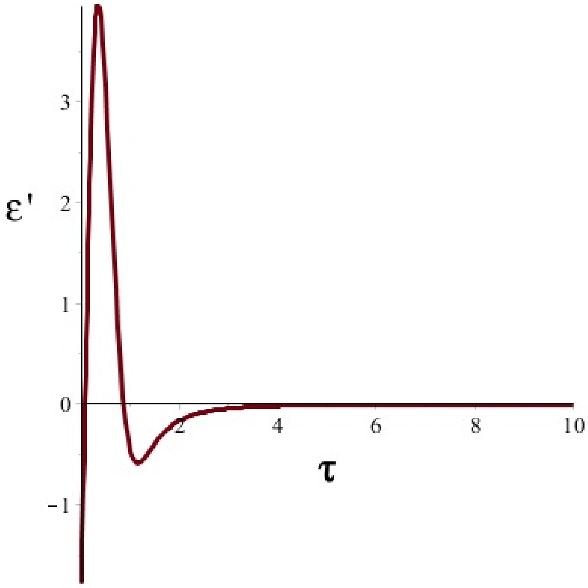

Figure 2. Real part of the dielectric function as a function of time.

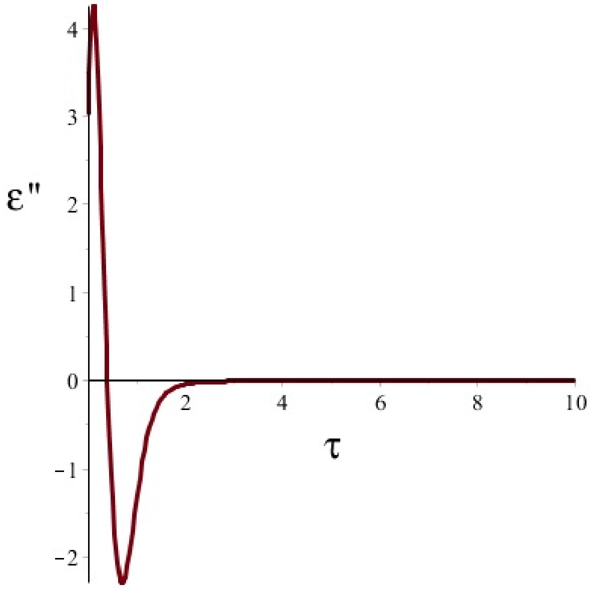

Figure 3. Imaginary part of the dielectric function as a function of time.

Here we denoted

$$W = \sigma_a \left(\frac{\varepsilon_b + 2}{3}\right)^2 \exp(-\frac{\Delta\omega^2}{2\sigma_{2s}})\tilde{J} \tag{23}$$

- the probability of the optical transitions induced by external field, and $\tau = Wt$ - dimensionless time. We put $WT_1 = 1000$. Figs.1, 2 and 3 illustrate non-steady-state near-zero dielectric permittivity. As population n_2 approaches to 1, dielectric permittivity approaches to zero.

4. APPLICATION TO EXCITON COMPENSATION OF COULOMB BLOCKING (ECCB) IN CONDUCTION NANOJUNCTIONS.

In Ref.[6] we studied the influence of both exciton effects and Coulomb repulsion on current in nanojunctions. We showed that dipolar energy-transfer interactions between the sites in the wire can at high voltage compensate Coulomb blocking for particular relationships between their values. Although in free exciton systems dipolar interactions J ($\lesssim 0.01 - 0.1 eV$[25]) are considerably smaller than on-site Coulomb interaction U (characteristically $U \sim 1$ eV[26]) the former may still have strong effects under some circumstances, e.g. in the vicinity of metallic structures in or near the nanojunctions. In such cases dipolar interactions may be enhanced. The enhancement of the dipole-dipole interaction calculated using finite-difference time-domain simulation for the dimer of silver spheres, and within the quasistatic approximation for a single sphere, reached the value of 0.13 eV for nanosphere-shaped metallic contacts[6] that was smaller than U. In addition, this enhancement was accompanied by metal induced damping of excitation energy.

In this section we show that purely organic materials characterized by low losses with near-zero dielectric permittivities will enable us easily to obtain $J \sim 1$ eV$\sim U$. We shall consider a nanojunction consisting of a two site quantum dot wire between two metal leads with applied voltage bias. The junction is found into organic material with dielectric permittivity ε. The quantum dots of the wire posses dipole moments $\mathbf{D}_1$ and $\mathbf{D}_2$. The point dipoles are positioned at points $\mathbf{r}_1$ and $\mathbf{r}_2$, respectively, and oscillate with frequency Ω. The interaction energy between dipoles 1 and 2 can be written in a symmetrized form as $J_{12} + J_{21}$ where

$$J_{12} = -\frac{1}{2}\mathbf{D}_1 \cdot \mathbf{E}_2(\mathbf{r}_1, \Omega, t), \ , \tag{24}$$

$$J_{21} = -\frac{1}{2}\mathbf{D}_2 \cdot \mathbf{E}_1(\mathbf{r}_2, \Omega, t), \ , \tag{25}$$

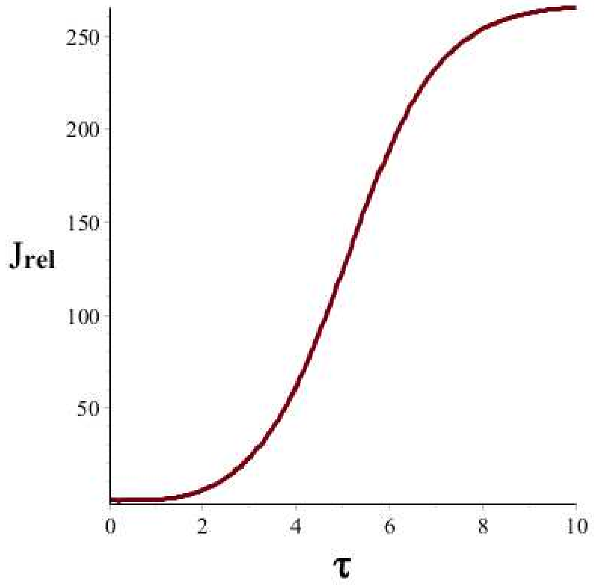

Figure 4. Enhancement of the dipole-dipole interaction in a medium with dielectric function $\varepsilon(\Omega, t)$ given by Figs.2 and 3.

$\mathbf{E}_2(\mathbf{r}_1, \Omega, t) \sim \mathbf{D}_2$ is the electric field at a point $\mathbf{r}_1$ induced by the dipole $\mathbf{D}_2$, etc.

The electric field is given by Coulomb's law

$$\mathbf{E}(\mathbf{r}, \Omega, t) = \frac{1}{\varepsilon(\Omega, t)} \int \rho_i(\mathbf{r}') \frac{\mathbf{r} - \mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|^3} d^3\mathbf{r}' \tag{26}$$

that corresponds to the electrostatic approximation. Such extension of the electrostatic formula is possible due slow changes in time of $\varepsilon(\Omega, t)$ (see above). Here the external charge density $\rho_i(\mathbf{r}')$ due to the presence of dipole $\mathbf{D}_i$ can be written as[27] $\rho_i(\mathbf{r}') = -\mathbf{D}_i \cdot \nabla_{\mathbf{r}'} \delta(\mathbf{r}' - \mathbf{r}_i)$ (we consider a point dipole positioned at point $\mathbf{r}_i$). One can show that $U_{12} = U_{21} \equiv \frac{1}{2}\hbar J(\Omega, t)$. This can be expected from the reciprocity theorem,[28] according to which the fields of two dipoles $\mathbf{D}_1$ and $\mathbf{D}_2$ at positions $\mathbf{r}_1$ and $\mathbf{r}_2$ and oscillating with the same frequency Ω are related as $\mathbf{D}_1 \cdot \mathbf{E}_2(\mathbf{r}_1, \Omega) = \mathbf{D}_2 \cdot \mathbf{E}_1(\mathbf{r}_2, \Omega)$. If the dipoles are oriented parallel to the symmetry axis of the junction,[29] the dipole-dipole interaction is given by

$$J(\Omega, t) = \frac{1}{\varepsilon(\Omega, t)} \frac{-2D_1 D_2}{|\mathbf{r}_1 - \mathbf{r}_2|^3} \tag{27}$$

One can define a magnitude

$$J_{rel} \equiv \left| \frac{J(\Omega, t)}{J_{vac}} \right| = \frac{1}{|\varepsilon(\Omega, t)|} \tag{28}$$

that shows the enhancement of the dipole-dipole interaction in a medium with dielectric function $\varepsilon(\Omega, t)$ with respect to that

$$J_{vac} = \frac{-2D_1 D_2}{|\mathbf{r}_1 - \mathbf{r}_2|^3} \tag{29}$$

in vacuum. Fig.4 shows J_{rel} as a function of time for a medium with dielectric function given by Figs.2 and 3. Here $J_{rel}(\tau = 0) = 0.2864$ and $J_{rel}(\tau = 10) = 265.6394$, so that the ratio $J_{rel}(\tau = 10)/J_{rel}(\tau = 0) = 927.5 \sim 10^3$. In other words, the enhancement is about 10^3 with respect to the equilibrium state. Putting $D_1 = D_2 = 25D$ and $|\mathbf{r}_1 - \mathbf{r}_2| = 5nm$, one gets $|J_{vac}| = 0.006\,25eV$, and the value of $|J(\Omega, t)| = 1.660\,2eV$ for $\tau = 10$.

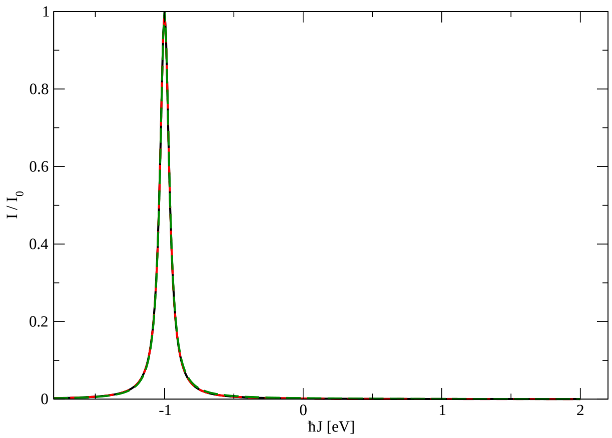

Figure 5. (Color online) Current I displayed as function of the energy-transfer coupling J for $U = 1\ eV$ and $\Delta_f = \Delta_{ff'} \equiv \Delta = 0.01eV$. The current shows a maximum at $U = -\hbar J$. Solid black line - calculations using Eqs.(30) and (31) for energy and electron transfer, respectively; red dashed line - calculations using Eqs.(30) and (33) for energy, and Eq.(31) for electron transfer; green dashed line - calculations using Eqs.(30) and (33) for energy, and Eqs.(31) and (34) for electron transfer. Comparison of these lines displays small effects of non-resonance contributions.

4.1 Calculation of current. Optical switches based on ECCB.

Let us calculate current through the two site quantum dot nanojunction described in the beginning of this section using approach of Ref.[6] where the dipole-dipole interaction between quantum dots of the wire is defined by Eq.(27). The Hamiltonian of the wire, Eq.(3) of Ref.,[6] contained both the energy

$$H_{exc-exc} = \hbar J(\Omega, t) b_1^\dagger b_2 + H.c. \tag{30}$$

and electron transfer interactions written in the resonance approximation

$$H_{el-el} = -\sum_{f=g,e} \Delta_f (\hat{c}_{2f}^\dagger \hat{c}_{1f} + \hat{c}_{1f}^\dagger \hat{c}_{2f}) \tag{31}$$

The operators $b_m^\dagger = c_{me}^\dagger c_{mg}$ and $b_m = c_{mg}^\dagger c_{me}$ are exciton creation and annihilation operators on the molecular sites $m = 1, 2$. The Hamiltonian of the Coulomb interactions is expressed as

$$H_{cou} = \frac{U}{2} \sum_{m=1,2} N_m (N_m - 1) \tag{32}$$

with $N_m = n_{mg} + n_{me}$. Since in the medium with near-zero dielectric permittivities both exciton-exciton interaction J and on-site Coulomb interaction U can achieve the value of about $1\ eV$ (see above), we account and add the additional two off-resonance terms to $H_{exc-exc}$ and H_{el-el} respectively, as

$$H_{non-exe-exe} = \hbar J(\Omega, t) b_1^\dagger b_2^\dagger + H.c.\ , \tag{33}$$

$$H_{non-el-el} = -\sum_{\substack{f,f'=g,e \\ f\neq f'}} \Delta_{ff'} (\hat{c}_{2f}^\dagger \hat{c}_{1f'} + \hat{c}_{1f'}^\dagger \hat{c}_{2f}) \tag{34}$$

Eq. 33 is so called non-Heitler-London term[30] taking into account creation and annihilation for excitation simultaneously at two sites (quantum dots). In this relation the following question arises: "does the effect of ECCB survive for such large values of $\hbar J \sim 1$ eV$\sim U$?"

Fig.5 shows that the ECCB does survive for large values of $J \sim 1$ eV. We put the bias voltage $V_{bs} = 8\ eV$ and the rate of charge transfer from a quantum dot to the corresponding lead $\Gamma = 0.02eV$ in our simulations, and denoted the unit of current as $I_0 = \dfrac{e\Gamma}{\hbar}$ (e is the charge of one electron). Fig.6 shows current through the

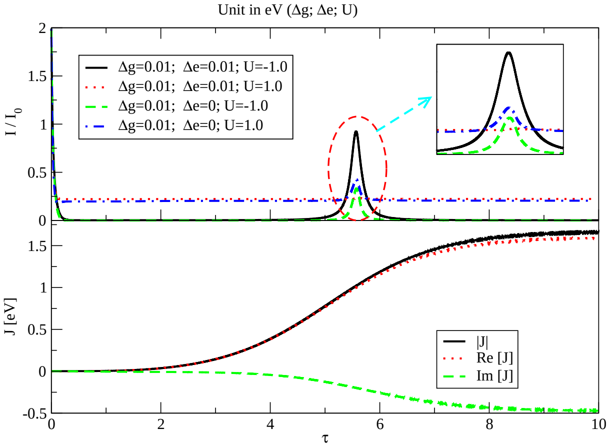

Figure 6. (Color online) Laser induced current I (top) and the dipole-dipole interaction in an organic material J (bottom) displayed as function of τ. Other parameters are identical to those of Figs.1, 2, 3 and 4

nanojunction during the action of the rectangular lase pulse with parameters given in Section3.1 on the host organic material.

One can see dramatic increasing the current when $\hbar J$ approaches to $-U$ for $\Delta_g = \Delta_e$, and to $\pm U$ for $\Delta_g \neq 0$ and $\Delta_e = 0$. After this moment the current decreases in spite of increasing J, since its value exceeds that of U. So, current exists during the time that is much shorter than the pulse duration. As a matter of fact, Fig.6 illustrates a new type of optical switches based on the effect of the exciton compensation of Coulomb blocking - ECCB switches.

5. CONCLUSION

In this work we have developed a theory of non-steady-state organic plasmonics with strong laser pulses that enable us to obtain near-zero dielectric permittivity during a short time. We have proposed to use non-steady-state organic plasmonics for the enhancement of intersite dipolar energy-transfer interaction in the quantum dot wire that influences on electron transport through nanojunctions. Such interactions can compensate Coulomb repulsions for particular conditions. We propose the exciton control of Coulomb blocking in the quantum dot wire based on the non-steady-state near-zero dielectric permittivity of the organic host medium, and a new type of optical switches - ECCB switches.

Our current calculations were carried out for a fixed value of $J(\Omega, t)$ corresponding to $\Omega = \omega_{21} - 2.040\,5\sqrt{2\sigma_{2s}}$. The extension of the calculations of current to frequency dependent $J(\Omega, t)$ will be made elsewhere.

ACKNOWLEDGMENTS

We gratefully acknowledge support by the US-Israel Binational Science Foundation (BF, grant No. 2008282).

REFERENCES

[1] L. Gu, J. Livenery, G. Zhu, E. E. Narimanov, and M. A. Noginov, "Quest for organic plasmonics," *Applied Phys. Lett.* **103**, p. 021104, 2013.

[2] T. U. Tumkur, J. K. Kitur, L. Gu, G. Zhu, and M. A. Noginov in *Abstracts of NANOMETA 2013*, p. FRI3o.6, Seefeld, Austria, 2013.

[3] B. D. Fainberg, "Nonperturbative analytic approach to interaction of intense ultrashort chirped pulses with molecules in solution: Picture of "moving" potentials," *J. Chem. Phys.* **109**(11), pp. 4523–4532, 1998.

[4] M. E. Crenshow, M. Scalora, and C. M. Bowden, "Ultrafast intrinsic optical switching in dense medium of two-level atoms," *Phys. Rev. Lett.* **68**, pp. 911–914, 1992.

[5] B. D. Fainberg and B. Levinsky, "Stimulated Raman Adiabatic Passage in a Dense Medium," *Adv. Phys. Chem.* **2010**, p. 798419, 2010.

[6] G. Li, M. S. Shishodia, B. D. Fainberg, B. Apter, M. Oren, A. Nitzan, and M. Ratner, "Compensation of Coulomb blocking and energy transfer in the current voltage characteristic of molecular conduction junctions," *Nano Letters* **12**, pp. 2228–2232, 2012.

[7] B. D. Fainberg and B. S. Neporent *Opt. Spectrosc.* **48**, p. 393, 1980. [Opt. Spektrosk., v. 48, 712 (1980)].

[8] B. D. Fainberg and I. B. Neporent *Opt. Spectrosc.* **61**, p. 31, 1986. [Opt. Spektrosk., v. 61, 48 (1986)].

[9] B. D. Fainberg and I. N. Myakisheva *Sov. J. Quant. Electron.* **17**, p. 1595, 1987. [Kvantovaya Elektron. (Moscow), v. 14, 2509 (1987)].

[10] B. D. Fainberg and I. N. Myakisheva *Opt. Spectrosc.* **66**, p. 591, 1989. [Opt. Spektrosk., v. 66, 1012 (1989)].

[11] B. D. Fainberg *Opt. Spectrosc.* **60**, p. 74, 1986. [Opt. Spektrosk., v. 60, 120 (1986)].

[12] R. F. Loring, Y. J. Yan, and S. Mukamel *J. Chem. Phys.* **87**, p. 5840, 1987.

[13] W. Vogel, D.-G. Welsh, and B. Wilhelmi *Phys. Rev. A* **37**, p. 3825, 1988.

[14] B. D. Fainberg *Opt. Spectrosc.* **65**, p. 722, 1988. [Opt. Spektrosk., vol. 65, 1223, 1988].

[15] S. Mukamel, *Principles of Nonlinear Optical Spectroscopy*, Oxford University Press, New York, 1995.

[16] V. V. Khizhnyakov *Izv. Akad. Nauk SSSR, Ser. Fiz.* **52**, p. 765, 1988.

[17] B. D. Fainberg *Opt. Spectrosc.* **58**, p. 323, 1985. [Opt. Spektrosk. v. 58, 533 (1985)].

[18] Y. J. Yan and S. Mukamel *Phys. Rev. A* **41**, p. 6485, 1990.

[19] B. D. Fainberg *Opt. Spectrosc.* **68**, p. 305, 1990. [Opt. Spektrosk., vol. 68, 525, 1990].

[20] B. Fainberg *Phys. Rev. A* **48**, p. 849, 1993.

[21] B. D. Fainberg *Opt. Spectrosc.* **67**, p. 137, 1989. [Opt. Spektrosk., v. 67, 241 (1989)].

[22] B. D. Fainberg, "Non-linear polarization and spectroscopy of vibronic transitions in the field of intensive ultrashort pulses," *Chem. Phys.* **148**, pp. 33–45, 1990.

[23] M. Abramowitz and I. Stegun, *Handbook on Mathematical Functions*, Dover, New York, 1964.

[24] A. A. Batista and D. S. Citrin, "Rabi flopping in a two-level system with a time-dependent energy renormalization: Intersubband transitions in quantum wells," *Phys. Rev. Lett.* **92**(12), p. 127404, 2004.

[25] S. Mukamel and D. Abramavicius, "Many-body approaches for simulating coherent nonlinear spectroscopies of electronic and vibrational excitons," *Chem. Rev.* **104**, pp. 2073–2098, 2004.

[26] H. Thomann, L. R. Dalton, M. Grabowski, and T. C. Clarke, "Direct observation of coulomb correlation effects in polyacetylene," *Phys. Rev. B* **31**(5), pp. 3141–3143, 1985.

[27] X. M. Hua, J. I. Gersten, and A. Nitzan, "Theory of energy transfer between molecules near solid particles," *J. Chem. Phys.* **83**(7), pp. 3650–3659, 1985.

[28] L. D. Landau and E. M. Lifshitz, *Electrodynamics of Continuous Media*, Pergamon Press, New York, 1960.

[29] M. S. Shishodia, B. D. Fainberg, and A. Nitzan, "Theory of energy transfer interactions near sphere and nanoshell based plasmonic nanostructures," in *Plasmonics: Metallic Nanostructures and Their Optical Properties IX. Proc. of SPIE*, M. I. Stockman, ed., **8096**, p. 8096 1G, SPIE, Bellingham, WA, 2011.

[30] A. S. Davydov, *Theory of Molecular Excitons*, Plenum, New York, 1971.