Light-induced “plasmonic” properties of organic materials: Surface polaritons and switching waves in bistable organic thin films

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Light-induced “plasmonic” properties of organic materials: Surface polaritons and switching waves in bistable organic thin films

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Purely organic materials with negative and near-zero dielectric permittivity can be easily fabricated, and the propagation of surface polaritons at the material/air interface was demonstrated. Here, we develop a theory of nonlinear light-induced “plasmonic” properties of organic materials. We predict the generation of switching waves or kinks in the bistable organic thin films that enable us to observe a bistable behaviour of the surface polaritons at the organic thin film/dielectric interface under laser irradiation. We present the alternating-sign dependence of the switching wave velocity on pump intensity and discuss a possibility of controlling the polariton propagation by switching waves. *Published by AIP Publishing.* [http://dx.doi.org/10.1063/1.4983561]

Plasmonics and metamaterials provide great scope for concentrating and manipulating the electromagnetic field on the subwavelength scale to achieve dramatic enhancement of optical processes and to develop super-resolution imaging, optical cloaking, etc.[1–4] However, 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.[5] Highly doped semiconductors[5,6] and doped graphene[7–9] can in principle solve the loss problem. However, the plasmonic frequency in these materials is an order of magnitude lower than that in metals making former most useful in mid-IR and THz regions. 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 wide technological fields of nanoplasmonics and metamaterials.

Recently, Noginov *et al.*[10] and Gentile *et al.*[11] demonstrated that purely organic materials characterized by low losses with negative, near-zero, and smaller than unity dielectric permittivities can be easily fabricated, and propagation of a surface polariton (SP) at the material/air interface was demonstrated. Even the dramatic laser-induced change in the dielectric permittivity of organic dyes may be realized[12,13] that can enable us to control their “plasmonic” properties. The experiments with strong laser pulses[12] challenge the theory.

In Ref. 13, we have developed a theory of the light-induced “plasmonic” properties of organic materials. Our consideration was based on the model of the interaction of strong (phase modulated) laser pulses with organic molecules, Ref. 14, extended to the dipole-dipole intermolecular interactions in the condensed matter. The latter was taken into account using a mean-field theory that resulted in two options:[13] one mother and two daughters. The first option correctly described the behaviour of the first moment of molecular spectra in condensed matter and specifically the redshift, according to the Clausius-Mossotti Lorentz-Lorenz (CMLL) mechanism.[15] The second option is related to the dramatic modification of molecular spectra in condensed matter and will be considered elsewhere. In any case, the mean-field theory resulted in essentially nonlinear equations for strong laser excitation that demonstrated a bistable behaviour of the electronic state populations n_j ($j=1$ and 2) as functions of the power density of the exciting radiation $\tilde{J}$.[16]

The phenomenon of bistability in spatially distributed systems acquires new important features well developed in optical bistability.[17,18] Among the key elements here are switching waves (SWs) or kinks responsible for such effects as spatial bistability, spatial hysteresis, and dissipative solitons.[18] The goal of this study is the search and investigation of the SW in the organic “plasmonic” materials and discussion of their connection with the SPs that may be considered here as exciton polaritons (this issue will be discussed in more detail elsewhere).

Let us consider molecules with two electronic states $n=1$ (ground) and 2 (excited) in a solvent. The molecules are affected by the radiation of power density $\tilde{J}$, the frequency of which is close to that of the transition $1 \to 2$. We shall consider the particular case of fast vibrational relaxation when the equilibrium distributions into the electronic states have had time to be set during the change in the pulse parameters. In that case, the dielectric function at frequency Ω can be written as[13]

$$\varepsilon(\Omega) = 1 + i\frac{4\pi^{3/2}|D_{12}|^2 N}{3\hbar\sqrt{2\sigma_{2s}}}\sum_{j=1,2}(-1)^{j+1}n_j(t) \times w\left(\frac{\Omega-\omega_{21}+p\Delta n+\delta_{2j}\omega_{st}}{\sqrt{2\sigma_{2s}}}\right) \qquad (1)$$

for the CMLL redshift in condensed matter. Here, σ_{2s} is the second central moment of an absorption spectrum, $\Delta n = n_1 - n_2 = 1 - 2n_2$, $p = \frac{4\pi}{3\hbar}|D_{12}|^2 N$ is the strength of the near dipole-dipole interaction, ω_{21} is the frequency of Franck-Condon transition $1 \to 2$, N is the density of molecules, δ_{2j} is the Kronecker delta, D_{12} is the electronic matrix element of the dipole moment operator, $\omega_{st}=\hbar\sigma_{2s}/(k_BT)$ is the Stokes shift of the equilibrium absorption and luminescence spectra, and $w(z)$ is the probability integral of a complex argument[19] whose real part describes absorption and the imaginary part describes refraction. The excited state population n_2 obeys nonlinear Eq. (3) of Ref. 13

$$dn_2/dt=-F(n_2),\qquad(2)$$

where

$$F(n_2)=\frac{n_2}{T_1}\left\{\left[1+\exp\left(-\frac{\hbar(\omega_{st}-2\Delta\omega)}{2k_BT}\right)\right]J\times\exp\left(-\frac{\Delta\omega^2}{2\sigma_{2s}}\right)+1\right\}-J\exp\left(-\frac{\Delta\omega^2}{2\sigma_{2s}}\right),\qquad(3)$$

$\Delta\omega=(\omega_{21}-\omega)-p(1-2n_2)$, T_1 is the lifetime of the excited state, $J=\sigma_a[(\varepsilon_b+2)/3]^2\tilde{J}T_1$, σ_a is the cross section at the maximum of the absorption band, and ε_b is the "bulk" relative permittivity (which can be due to distant high-frequency resonances of the same absorbing molecules or a host medium). Eqs. (1)–(3) make it clear as the excited state population increases, the spectrum exhibits a blueshift that should essentially contribute to the absorption. As a matter of fact, the bistable behavior of the population arises from the dependence of the resonance frequency of the molecules in the dense medium on the number of excited molecules.[16]

Since $\varepsilon(\Omega)$ depends on the electronic state populations n_j, the bistable behaviour of the population results in the bistable behavior of $\varepsilon(\Omega)$. Figure 1 shows the real part of $\varepsilon(\Omega)$, ε', for $(\Omega-\omega_{21})/\sqrt{2\sigma_{2s}}=-1.842$ calculated using Eq. (1), as a function of the power density of the exciting radiation related to the corresponding curve for the excited state population n_2 of Fig. 4, Ref. 16, at dimensionless detuning $(\omega_{21}-\omega)/\sqrt{2\sigma_{2s}}=0.25$. The lower and upper branches of the curve for ε' correspond to the lower and upper stable branches, respectively, of the curve for n_2 in Fig. 4 of Ref. 16.

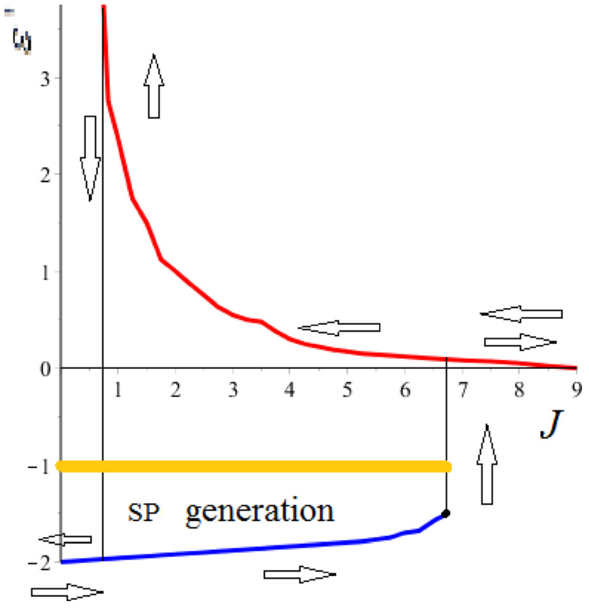

FIG. 1. Dependence of ε' on power density of the exciting radiation $\tilde{J}$ for $\varepsilon_b=1$. The arrows pointing right show the ε' behaviour when $\tilde{J}$ increases, and the arrows pointing left show the ε' behaviour when $\tilde{J}$ decreases. The vertical arrows point to the jumps between the lower and upper stable branches. The SP excitation is possible only below the horizontal thick line at $\varepsilon'=-1$.

Indeed, the excitation of SPs at the organic thin film/air interface is possible for substantially strong negative values of dielectric function $\varepsilon(\Omega)$,[10,20] and therefore, only the lower branch will correspond to the SP generation. In this relation, the following question arises: how can one observe a bistable behaviour of SPs at the organic thin film/air interface under laser irradiation? This can be achieved with the aid of transverse phenomena such as SWs known in optical bistability.[18] The SWs were initiated by radiation heating of the semiconductor rod. The point is that the absorption coefficient of a semiconductor increases with temperature. A similar dependence of the absorption coefficient of the molecules in the dense medium on the power density of exciting radiation can be realized on the excitation at the blue side of the absorption spectrum.[16] Because of this, one can expect the generation of SWs also in the organic films under consideration, although the mechanism of bistability is essentially different from that of a semiconductor.

Let us suppose that the organic thin film is irradiated with a strong field (pump) falling perpendicular to its surface (and the coordinate x that is parallel to the film surface) (Fig. 2). The point is that in the case of bistability, the steady-state distribution of the excited state population n_2 may be inhomogeneous with respect to x at the definite value of the power density of exciting radiation $\tilde{J}$ named the Maxwell value $\tilde{J}_M$,[18] even though $\tilde{J}$ does not depend on x (plane wave). For an arbitrary value of $\tilde{J}$, the distributions under discussion become non-steady-state ones, resulting in the SWs.[18] In our case, the SW will be related to the excitation (population n_2) profile propagating along the organic film. To analyze such SWs, we should take the excitation transfer along the organic film due to intermolecular interactions into account. Using phenomenological diffusional approach[21] and Eq. (2), one can write

$$\frac{\partial n_2}{\partial t}=D\frac{\partial^2 n_2}{\partial x^2}-F(n_2),\qquad(4)$$

where D is the diffusional coefficient that can be expressed in terms of the strength of the near dipole-dipole interaction p

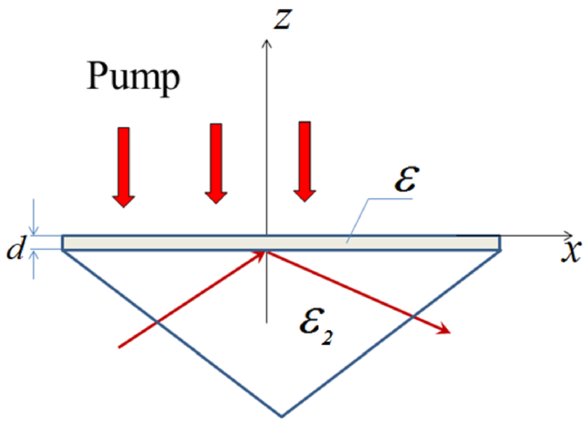

FIG. 2. Experimental configuration. The organic film with the dielectric function ε depending on the pump (thick arrows) contacts the dielectric prism. SPs are excited with an external weak p-polarized electromagnetic field (thin arrow) propagating in the dielectric prism (Kretschmann-Raether configuration).[20]

$$D = 0.171\frac{p^2}{N^{2/3}}T'. \tag{5}$$

Here, T' is the irreversible dephasing time of the electronic transition.[14] The above mentioned steady-state spatially inhomogeneous distribution of the excited state population n_2 corresponding to the Maxwell value of the exciting radiation $\tilde{J}_M$ is the solution of the steady-state diffusional equation, Eq. (4), when $\partial n_2/\partial t = 0$. The SWs $n_2 = n_2(x - vt)$ are the solutions of non-steady-state Eq. (4) for the boundary conditions at the edges of the sufficiently long, as compared with the width of SWs, organic film corresponding to the values of n_2 related to different branches of the function $n_2(\tilde{J})$ showing the bistable behaviour. They are displayed in Fig. 3 for the values of parameters close to those of molecule LD690:[14] $\sqrt{\sigma_{2s}} = 546\,\text{cm}^{-1}$, $T' = 2.5\times10^{-14}\text{s}$, $D_{12} = 10^{-17}$ CGSE that gives $\omega_{st} = 1420\,\text{cm}^{-1}$, $p = 2107\,\text{cm}^{-1}$. We also used $\varepsilon_b = 1$ and $N = 10^{21}\text{cm}^{-3}$,[10] and we got $D = 6.7\,\text{cm}^2/\text{s}$.

We have also checked that the diffusional approximation is correct.

Figures 4 and 5 show the profiles of SWs corresponding to maximal velocities and the velocities as functions of the power density of the exciting radiation for $(\omega_{21} - \omega)/\sqrt{2\sigma_{2s}} = 0.25$ (the bistability range $J = 0.72$–6.92) and 0.5 (the bistability range, $J = 0.594$–2.415), respectively. The corresponding values of $\tilde{J}\left[\frac{photons}{\text{cm}^2\,\text{s}}\right] = J/(\sigma_a T_1)$ can be obtained by multiplying J by $10^{25}\left[\frac{photons}{\text{cm}^2\,\text{s}}\right]$ for $\sigma_a \approx 10^{-16}$ cm^2.[13] One can see the alternating-sign dependence of the switching wave velocity on pump intensity. The zero values of the SW velocities correspond to the Maxwell value of the exciting radiation $\tilde{J}_M$ ($= 0.978\times10^{25}\left[\frac{photons}{\text{cm}^2\,\text{s}}\right]$ for Fig. 4 and $0.743\times10^{25}\left[\frac{photons}{\text{cm}^2\,\text{s}}\right]$ for Fig. 5). If $\tilde{J} > \tilde{J}_M$, the SW moves right ($v > 0$). If $\tilde{J} < \tilde{J}_M$, the SW moves left ($v < 0$).

By evaluating the maximal velocity $\bar{v}_{\max} \simeq \sqrt{D/T_1}$ and the wavefront width $\sqrt{DT_1}$ of the SW (Ref. 18) (see also supplementary material), one gets $\bar{v}_{\max} \simeq 8.2\times10^4\,\text{cm/s}$ and $\sqrt{DT_1} \simeq 8.2\times10^{-5}$cm for the used values of the parameters, where $T_1 = 10^{-9}$s. The transverse width of the thin film should be considerably larger than the wavefront width, i.e., 1 μm. One can see that in reality, the maximal velocity is nearly twice or triple as large as $\bar{v}_{\max}$.

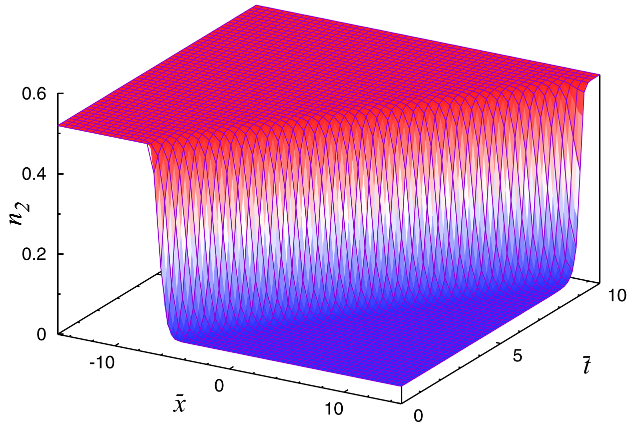

FIG. 3. SW for $(\omega_{21} - \omega)/\sqrt{2\sigma_{2s}} = 0.5$ and $J = 2.4$ as a function of dimensionless coordinate $\bar{x} = x/\sqrt{DT_1}$ and time $\bar{t} = t/T_1$, where $\sqrt{DT_1}$ is the diffusion path length.

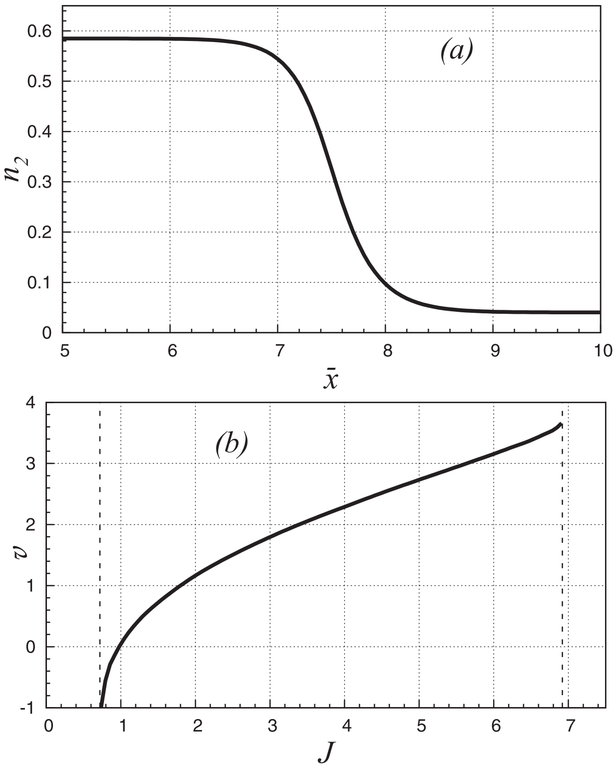

FIG. 4. Instantaneous profile (a) at $J = 6.91$ and velocities (b) of the SW. Detuning $(\omega_{21} - \omega)/\sqrt{2\sigma_{2s}}$ is equal to 0.25. The velocity is given in terms of $\bar{v}_{\max}$.

As a matter of fact, in the case under consideration, SW represents the wave of the dramatic change in the dielectric

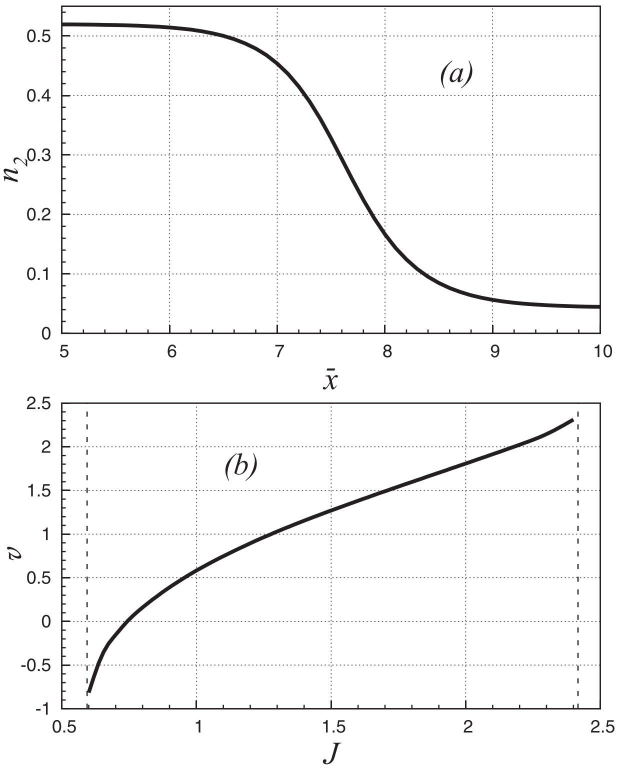

FIG. 5. Instantaneous profile (a) at $J = 2.4$ and velocities (b) of the SW. Detuning $(\omega_{21} - \omega)/\sqrt{2\sigma_{2s}}$ is equal to 0.5. The velocity is given in terms of $\bar{v}_{\max}$.

permittivity of organic dye films (experimentally, the laser-induced change in the dielectric permittivity of dye nanoparticles of the order of unity observed in Ref. 12). This may have many applications including addressing the theoretical predictions of the quantum field theory in time-dependent environments.[22]

Specifically, since only the lower branch of the bistability curve will correspond to the SP generation (see above and Fig. 1), the SWs offer the prospect of the optical manipulation of the SPs. Indeed, the range of existing SPs in Figs. 4 and 5 increases or decreases depending on whether the SW propagates to the left or the right. Moreover, because the wavenumber of the SP is equal to $k_x = \Omega/v_{SP} = \frac{\Omega}{c}\sqrt{\frac{\varepsilon(\Omega)\varepsilon_2}{\varepsilon_2+\varepsilon(\Omega)}}$ where $\varepsilon_2 > 0$ is the dielectric constant of an adjacent dielectric,[3,20] the SP velocity is given by $v_{SP} = c\sqrt{1/\varepsilon_2 + 1/\varepsilon(\Omega)}$. It dramatically slows down at resonance $\varepsilon(\Omega) \approx -\varepsilon_2$ and may be of the same order of magnitude as the velocity of the SW, $\bar{v}_{\max}$. In such a situation, one can speak, among other processes, about collisions between SPs and SWs. This issue will be considered elsewhere.

See supplementary material for additional information on SWs, the derivation of the relationship between the diffusion coefficient and the strength of near dipole-dipole interactions, and evaluations of the SW velocity and the wave front width. In addition, it also includes a video clip showing the SW propagation in real time.

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