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Controlled Optical Transition Rates in Nanodroplets

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<u>SUMMARY</u>

Spontaneous emission of light arising from atomic and/or molecular systems is a major natural optical phenomenon. Ability to control spontaneous emission of light has recently drawn attention because of potential technological applications such as lasers with lower thresholds to initiate lasing.

Reverse micellar systems consisting of nano-sized droplets of nonaqueous polar solvents, dispersed in an oil-continuous phase have potential as novel reaction media. Recently, the possibility of superradiant emission at visible wavelength from cyanine aggregates at interfaces is presented[1-3]. The spectroscopy and dynamics of cyanine dyes at interfaces of confined systems is intriguing due to the promise of new materials having controlled optical properties.

We report time-resolved fluorescence measurements of 3,3'-diethyl-5,5'-dichloro-9-phenylthiacarbocyanine (DDPT) in bulk solvents and methanol-in-oil reverse micellar systems which include nano-sized methanol droplets stabilised with anionic surfactant aerosol-OT (AOT) in n-heptane, at room temperature. DDPT has no solubility in the n-alkane phase of m/o reverse micellar systems. It is therefore reasonable to assume that the dye solved in methanol is incorporated within the droplet. The regions available to the dye include the core of the dispersed droplet, as well as the interfacial region which is highly ionic due to the anionic head-groups of the AOT molecules and the counter ions in the Stern layer It is expected that due to strong electrostatic interactions with the anionic head-groups, the positively charged DDPT should locate itself at the interfacial region. Relative fluorescence intensities of DDPT increase with a factor of 16 in m/o reverse micelles in comparison to those in bulk methanol. The fluorescence lifetimes in m/o reverse micelles vary between 1.5 to 2.2 ns as a function of size of the dispersed methanol droplets, whereas in bulk methanol 75 ps of fluorescence lifetime is measured. The radiative and non-radiative rate constants for DDPT decreases in methanol dispersions, indicating that internal motions of DDPT in these droplets is reduced due to strong electrostatic interactions between the positively charged DDPT and the negatively charged sulfonate head-groups of AOT and spatial confinement by the reverse micellar structure.

We are able to control optical transition rates utilising m/o reverse micellar structures and show that reverse micelles would be a candidate as molecular tools to prepare light emitting materials having controlled optical properties.

Table 1: Photophysical parameters of DDPT methanol-in-oil reverse micelles.

W_o	τ_{fluo}(ns) χ^2	ϕ_{fluo}	k_rx10^9(s^{-1})	k_{nr}x10^9(s^{-1})	k_r^{rv}/k_r^{bulk}	$k_{nr}^{rv}/k_{nr}^{bulk}$	k_{nr}/k_r
2	1.52 (1.3)	0.25	0.17	0.49	0.82	0.037	3
4	1.68 (1.3)	0.25	0.15	0.45	0.74	0.034	3
6	2.21 (1.2)	0.25	0.11	0.34	0.56	0.026	3
MeOH	0.075 (0.8)	0.015	0.20	13.10	-	-	65
EG	0.55 (1.2)	0.066	0.12	1.70	-	-	14
GLY	2.04 (0.8)	0.105	0.05	0.45	-	-	9

References:
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Superfocusing of plasmon polariton on rough surface of metal: theory and experiment

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It is well known that the roughness of the metal surface promotes the enhancement of the nonlinear optical response. It may be suggested that the increase of the wave field is caused by the excitement of the surface plasmon polaritons. However, up to now the peculiarities of the formation of polariton modes and causes of the anomalous growth of the wave fields have not been investigated.

In the previous work [1] we shown, that the necessary conditions exist for the strong localization of the wave and anomalous increase of electric fields in the process of propagation of the surface polariton through the wedge–like structure. The obtained results were valid for both the metallic structure of the wedge form and the structure of a metallic gap of wedge–like form. The mentioned effect of superfocusing of the surface plasmon polariton is general and can be observed not only in case of wedge–like structure.

In the present work we consider the structure, which consists of two identical metallic cones, contacting by their tips. (see figure).Theoretical consideration shown, that in the media with mentioned structure the surface plasmon polariton has the following principal features: in approaching to the contacting point the wave vector of the polariton infinitely increases by the law of $\sim 1/r$, where r is distance to contact point and, according by its wavelength decreases. Then, the diffraction phenomena do not limit the localization of the wave in very small region of the space. As a result, the wave fields anomalously grow ($H_\varphi \sim r^{-1/2}$, $E_r, E_\theta \sim r^{-3/2}$). The combination of these two features presents the essence of the superfocusing of the surface polariton.

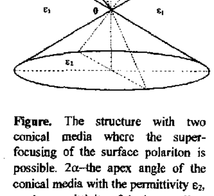

Figure. The structure with two conical media where the super-focusing of the surface polariton is possible. 2α–the apex angle of the conical media with the permittivity ε_2, ε_1–the permittivity of the intermediate dielectric medium.

In the experimental study we proceed from the supposition, that the mechanical contact between two pressed silver layers can be realized in separate points like presented in figure, that is the result of surface roughness, which have nanometric dimensions in case of mirror surface. The simplest result of the superfocusing can be the photodamage of the surface in the neighborhood of contact points.

The layer of silver on the surface of glass plate was prepared by evaporation in vacuum. The thickness of the silver layer was about 500nm, which provided its semitransparence. The samples, which are not photodamaged after 40-50 pulses with parameters: λ= 1064 nm, pulse energy –5mJ, pulse duration – 33ps were chosen. After that, the pare of selected layers were mechanically pressed and irradiated again in the same experimental conditions. The laser radiation was directed to this structure perpendicularly to the planes of metal layers. In this case the strong phothodamages were observed. Note here, that characteristic dimensions of the air space between pressed silver layers were less, than the wavelength of the laser radiation. Hence, the increase of the wave fields, which leads to the photodamages, can not be stipulated by the interference phenomena. We suggest that the phenomenon is the result of the surface plasmon polariton excitation. And, as the theoretical analysis shows, the localization of the polariton in the neighborhood of contact points leading to an anomalous increase of the wave fields is possible. The phenomenon explains the photodamage of the metal layers, observed in experiment.

[1] Kh.V. Nerkararyan, *Phys. Lett.* A237, 103, 1997.