Giant nonlinear susceptibility of thin films with (molecular *J*-aggregate)–(metal cluster) complexes

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The nonlinear susceptibility of films containing *J*-aggregates of a dye has been observed to increase significantly upon the incorporation of clusters of noble metals. The magnitude and dispersion of the nonlinear cubic susceptibility of the composite medium have been measured near an exciton transition of the *J*-aggregates.

One promising path for increasing the optical nonlinearities of substances is to form aggregates of microscopic particles or molecules in them. Examples are the increase by a factor of 10^6 in the efficiency of parametric four-wave mixing upon the agglomeration of Ag hydrosols into clusters[1] and the increase by several orders of magnitude in the susceptibility upon the formation of *J*-aggregates in solutions of organic dyes.[2] Butenko *et al.*[3] have predicted a significant increase in the nonlinear susceptibility of molecules adsorbed on fractal metal clusters, as the result of an increase in the local electric field in the clusters. Of particular interest for nonlinear optics is a composite of particles with a high intrinsic nonlinearity with metal clusters, which lead to a significant strengthening of the local field. In this letter we are reporting the observation of high-efficiency four-wave mixing in films of *J*-aggregates of pseudoisocyanine (PIC) in a solid polyvinylpyrrolidone (PVP) matrix and a significant increase in the nonlinear susceptibility of a film when clusters of gold or silver are added to it.

The perchlorate of PIC was synthesized by a procedure like that of Ref. 4 and was purified by recrystallization from acetonitrile. A polymer composition was prepared by dissolving PIC in a 20% acetonitrile solution of PVP to a concentration of 8×10^{-3}M. The formation of *J*-aggregates was stimulated by adding $K_2B_{10}H_{10}$ to the solution in a salt concentration of 6×10^{-3}M. This solution was then transferred to cover glasses by a centrifuging method. A colloidal solution of gold (or silver) obtained by reducing chloroauric acid (or $AgNO_3$) with sodium borohydride was added to some of the samples before the centrifuging.

Figure 1 shows absorption spectra of the films. We can clearly see peaks corresponding to an excitonic absorption of the *J*-aggregates of PIC ($\lambda\approx575$ nm).[5] Film 1 contains *J*-aggregates of PIC, while film 2 contains *J*-aggregates of PIC and gold clusters. Curve *3* in Fig. 1 is the absorption spectrum of a control film of PVP with

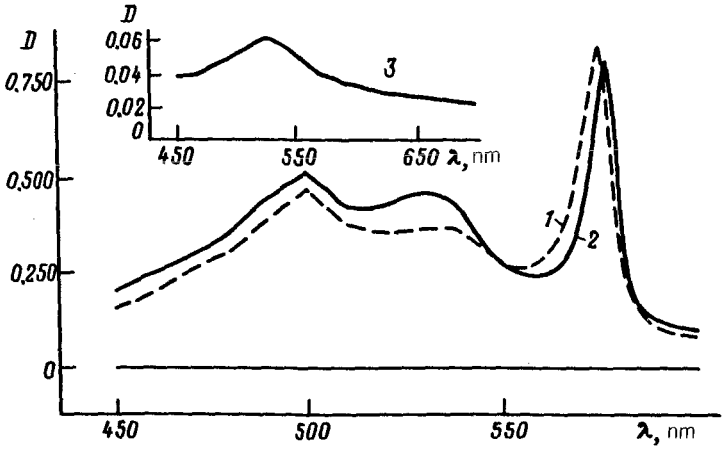

FIG. 1. Absorption spectra of films of *J*-aggregates of PIC. *1*—*J*-aggregates of PIC, $l = 1.5$ μm; *2*—*J*-aggregates of PIC with gold, $l = 4.0$ μm, $n_g = 10^{-2}$M. Curve *3* in the inset corresponds to gold in PVP with $l = 4.0$ μm and $n_g = 10^{-2}$M.

microscopic Au particles without a dye. The shape of curve *3* is typical of samples containing clusters consisting of microscopic gold particles ~ 5 Å in diameter.[6]

The nonlinear susceptibility $|\chi^{(3)}|$ was measured by nonlinear four-wave spectroscopy with biharmonic pumping.[7] In these experiments we used two dye lasers (the dye was rhodamine 6G), pumped by a common nitrogen laser. The frequencies of the laser beams were tuned independently; the polarizations of the beams were identical and linear. The typical output power of each of the lasers was 1–2 kW at a pulse length $2\tau \sim 5$ ns; the width of the spectra did not exceed $\Delta\omega_L = 0.5$ cm^{-1}. The light beams were spatially filtered and directed to the film with the *J*-aggregates of PIC by a lens ($F = 60$ cm) at an angle $\sim 1°$. The area of the spot at the e^{-2} level was $S \sim 10^{-4}$ cm^2. The frequency of one of the lasers (ω_1) was tuned to the center of the absorption line of the PIC *J*-aggregates (ω_J), while the frequency of the other laser (ω_2) was swept. After passage through the film, the light at the frequency $\omega_3 = 2\omega_1 - \omega_2$ which was generated was singled out by a diaphragm and sent to a DFS-452 spectrograph with a linear dispersion ~ 50 cm^{-1}/mm. The signal was selected by a slit at the exit from the spectrograph and detected by a photomultiplier. The dispersion of the nonlinear susceptibility $\chi^{(3)}$ was found from measurements of the energy efficiency η and the formula

$$\eta = \frac{W_3}{W_2} \approx \frac{2^{12}\pi^5}{c^2\lambda_3^2 n_1^2 n_2 n_3} \cdot \frac{10^{-D_3}\ln 2 W_1^2}{\sqrt{3}\times 2.3^2 S^2\tau^2(2D_1 + D_2 - D_3)^2}|\chi^{(3)}|^2 l^2,$$

where W_i is the energy of the light at the frequency ω_i, and n_i and D_i are the refractive index and optical density of the film at the frequency ω_i. The shapes of the pulses and the beam profiles were assumed to be Gaussian. It was assumed that D_i was close to 1. The film thicknesses, $l \sim 1$–4 μm, were measured with an MII-4 micrsocope. The

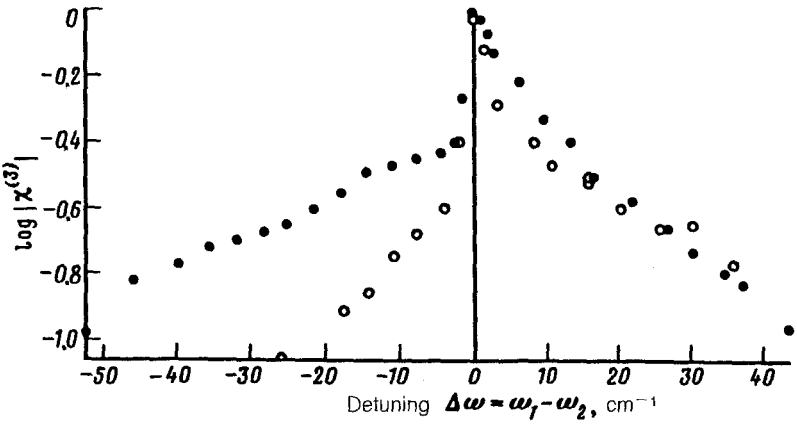

FIG. 2. Dispersion of the normalized values of $|\chi^{(3)}|$. ●—*J*-aggregates of PIC; ○—*J*-aggregates of PIC with gold.

refractive index n_i was calculated from measurements of the reflection and transmission coefficients of the films[8] near the frequency ω_J. We found $n(\omega \approx \omega_J) \approx 1.8$.

Figure 2 shows the results of the $|\chi^{(3)}|$ measurements as a function of $\Delta\omega = \omega_1 - \omega_2$ ($\omega_1 = \omega_J$). The nonlinear susceptibility reaches a maximum in the case $\Delta\omega = 0$. For the films with the PIC *J*-aggregates (spectrum 1 in Fig. 1), we found $|\chi_1^{(3)}(\Delta\omega = 0)| \approx 0.8 \times 10^{-7}$ cm^3/erg [a value $|\chi^{(3)}(\Delta\omega \approx 1\ \text{cm}^{-1})| \approx 10^{-7}$ cm^3/erg was measured in Ref. 2].

The introduction of metal clusters (Ag,Au) in a film with *J*-aggregates results in an increase in the efficiency of the nonlinear conversion. This increase in efficiency itself increases as the concentration of the metal in the sample is raised. For example, while a susceptibility of 5×10^{-7} cm^3/erg is found at a gold concentration $n_g = 10^{-3}$M, the value of $|\chi_2^{(3)}(\Delta\omega = 0)|$ at $n_g = 10^{-2}$M is $\sim 25 \times 10^{-7}$ cm^3/erg. This figure is 30 times that in a corresponding sample with *J*-aggregates but without metal clusters. We found this value at laser linewidths $\Delta\omega_L = 0.5$ cm^{-1}. Because of the sharp decay in $|\chi^{(3)}(\Delta\omega)|$, we would expect higher values of the susceptibility with decreasing $\Delta\omega_L$. The measured value of $|\chi_2^{(3)}(\Delta\omega = 0)|$ for a film with gold clusters (without the dye) is no greater than 5×10^{-10} cm^3/erg. The decay in $|\chi_3^{(3)}|$ with increasing $\Delta\omega$ is sharper than in sample 1 or 2. The conversion efficiency in the composite film reaches $\eta = 2 \times 10^{-4}$ at $I_1 \sim 170$ kW/cm^2. At $I_{1,2} < 170$ kW/cm^2, we observe a dependence $I_3 \propto I_1^2 I_2$. At higher intensities, the dependence is weaker at small detunings.

The high efficiency of the four-wave mixing at detunings $|\Delta\omega| < 50$ cm^{-1} is evidence of a short rise time of the nonlinear response of these samples. The $|\chi_1^{(3)}(\Delta\omega)|$ dependence at $\Delta\omega > 0$ in Fig. 2 is approximately the same as that measured for a solution of *J*-aggregates of PIC in Ref. 2, where a two-level model[9] was used to find the dephasing time of the exciton transition, $T_2 \simeq 0.17$ ps, from this dependence. As we

see from Fig. 2, however, the $\chi^{(3)}(\Delta\omega)$ dependence is asymmetric. Accordingly, caution should be exercised in using the two-level model of *J*-aggregates to find values of T_2. The theoretical study in Ref. 10 shows that two-photon transitions in *J*-aggregates can contribute substantially to the nonlinear susceptibility, along with the one-photon transition.

The increase in the nonlinear susceptibility of *J*-aggregates upon the addition of metal clusters to the matrix which we have observed here may be due to an increase in the fluctuating local electric field near "resonant" monomers of clusters.[1,3] According to this interpretation, the strengthened field acts on only a small fraction of the *J*-aggregates—a fraction close in order of magnitude to the volume fraction of gold in the sample, $f \sim 10^{-5}$–10^{-4}. This fraction of the aggregates is responsible for the increase by a factor of more than 30 in the susceptibility, averaged over the volume, found in our measurements. It follows from the data of Ref. 1 that the local field can exceed the incident field by a factor $\Lambda \sim 10$ in the case of metal clusters. The four-wave-mixing signal from the region of elevated field increases nonlinearly by a factor $\Lambda^{2n} = 10^6$ in this case (where $n = 3$ for four-wave mixing).

A detailed study of some new composite nonlinear media will be carried out in the future. However, it can be asserted even at this point that the film complexes of *J*-aggregates with gold clusters, which were synthesized and studied in the present work, have a significant nonlinear susceptibility, $\sim 2.5 \times 10^{-6}$ cm^3/erg, and a subpicosecond response time. These complexes are therefore interesting physical entities and hold promise for applications in optical devices.

[1]S. G. Rautian, V. P. Safonov, P. A. Chubakov *et al.*, Pis'ma Zh. Eksp. Teor. Fiz. **47**, 200 (1988) [JETP Lett. **47**, 243 (1988)].
[2]V. L. Bogdanov, E. N. Viktorova, S. B. Kulya, and A. S. Spiro, Pis'ma Zh. Eksp. Teor. Fiz. **53**, 100 (1991) [JETP Lett. **53**, 105 (1991)].
[3]A. V. Butenko, V. M. Shalaev, and M. I. Shtokman, Zh. Eksp. Teor. Fiz. **94**(7), 109 (1988) [Sov. Phys. JETP **67**, 1358 (1988)].
[4]J. Sondermann and Liebigs, Ann. Chem. **749**, 183 (1971).
[5]S. De Boer and D. A. Wiersma, Chem. Phys. Lett. **165**, 45 (1990).
[6]Yu. E. Danilova, A. I. Plekhanov, and V. P. Safonov, Physica A **61**, 185 (1992).
[7]T. Yajima and H. Souma, Phys. Rev. A **17**, 309 (1978).
[8]G. Hass and R. E. Thun (editors), *Physics of Thin Films, Vol. 2,* Academic, New York, 1964.
[9]T. Yajima, Opt. Commun. **14**, 378 (1975).
[10]F. S. Spano and S. Mukamel, J. Chem. Phys. **95**, 7526 (1991).

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