

Nonlinear cubic susceptibility and dephasing of exciton transitions in molecular aggregates

V. L. Bogdanov, E. N. Viktorova, S. V. Kulya, and A. S. Spiro
S. I. Vavilov State Optics Institute, 199164, Leningrad

(Submitted 20 December 1990)

Pis'ma Zh. Eksp. Teor. Fiz. **53**, No. 2, 100–103 (25 January 1991)

The magnitude and dispersion of the nonlinear cubic susceptibility $\chi^{(3)}$ have been measured for an exciton transition of J aggregates of pseudoisocyanine in liquid solutions. There is a pronounced increase in $\chi^{(3)}$ during the aggregation of the molecules. The dephasing time of the exciton transition, the absorption cross section, and the concentration and size of the "optical" aggregates have been determined.

A delocalization of an electronic excitation in a molecular aggregate leads to the formation of intense exciton resonances, near which we would expect an optical susceptibility higher than that of monomer structures.^{1,2} In fact, the absorption cross section of J aggregates³ of pseudoisocyanine (PIC) is estimated⁴ to be an order of magnitude greater than that of PIC molecules. A significant increase in the second-order nonlinearity during the aggregation of molecules of a thiapyrylium dye was observed in Ref. 5. We have measured the magnitude and dispersion of the cubic susceptibility $\chi^{(3)}$ of uncooled liquid solutions of J aggregates of PIC. We have found that $\chi^{(3)}$ increases sharply during aggregation, approaching record-high values for nonlinear optical media. From the experimental data we found the parameters which determine the optical susceptibilities of the aggregates: the dephasing time of the exciton transition and an upper boundary on the number of molecules in the exciton region (the size of an "optical" aggregate).

We studied solutions of J aggregates of PIC chloride in D_2O with an initial molecular concentration $N \approx 1.6 \times 10^{18} \text{ cm}^{-3}$ in a cell $l = 20 \mu\text{m}$ thick at room temperature. Figure 1 shows the absorption spectrum of the working solution in the region of the exciton resonance (the frequency of the maximum is $\nu_m \approx 17\,460 \text{ cm}^{-1}$). The $\chi^{(3)}$ measurements were carried by four-wave mixing⁶ during biharmonic pumping by narrow-band laser beams at frequencies ν_1 and ν_2 (the spectral width of the pump beams was $< 0.3 \text{ cm}^{-1}$). The dispersion of $\chi^{(3)}$ was found from the behavior of the intensity (I_c) of the four-wave mixing signal ($|\chi^{(3)}| \sim \sqrt{I_c}$) at the frequency $\nu_c = 2\nu_1 - \nu_2$ as a function of the detuning $\Delta\nu = \nu_1 - \nu_2$. The procedure for measuring the $|\chi^{(3)}(\Delta\nu)|$ spectra is described in more detail in Ref. 7.

Figure 2 shows experimental data on $|\chi^{(3)}(\Delta\nu)|$ for $\nu_1 \approx \nu_m$ and for various pump power levels $I_1(\nu_1)$ and $I_2(\nu_2)$. The behavior of $|\chi^{(3)}|$ as a function of I_1 and I_2 at small values of the frequency deviation (Fig. 2) can be explained on the basis of saturation effects, as in Ref. 6, and also on the basis of singlet-singlet annihilation.⁴ According to our measurements, however, this dependence is not seen in the region $\Delta\nu \gtrsim 5 \text{ cm}^{-1}$,

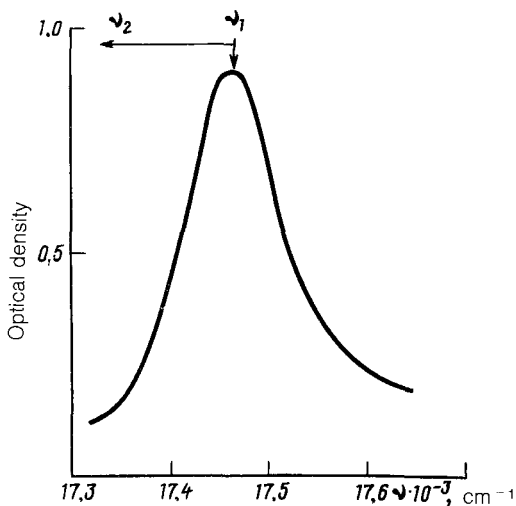


FIG. 1. Absorption spectrum of the working solution (at 20 °C). The arrows show the position of the frequency ν_1 and the direction and the interval of the turning of the frequency ν_2 .

with $I_1 \approx I_2 \lesssim 200 \text{ kW/cm}^2$. It was thus possible to eliminate from consideration an effect of the excitation power level on the shape of the $|\chi^{(3)}(\Delta\nu)|$ curve under these conditions.

The small width of the absorption spectrum ($V \approx 130 \text{ cm}^{-1}$; Fig. 1) and the

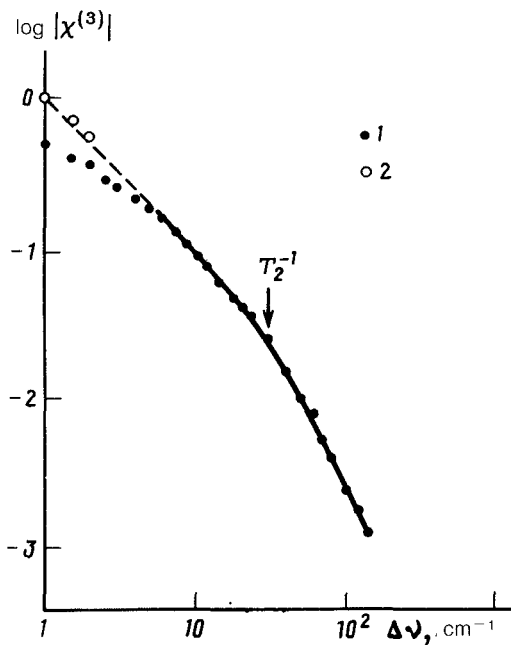


FIG. 2. Dispersion of $|\chi^{(3)}|$. The excitation intensity is (1) $I_1 \approx I_2 \approx 180 \text{ kW/cm}^2$ or (2) $I_1 \approx I_2 \approx 14 \text{ kW/cm}^2$. The curve is an approximation by Eq. (1).

circumstance that the band of the resonant fluorescence of the J aggregates essentially coincides with this spectrum⁴ show that the coupling of the electronic transitions with nuclear vibrations weakens substantially in the course of the aggregation. This circumstance, which indicates a similarity between J aggregates and atomic systems, makes it possible to use the theory of four-wave mixing derived in Ref. 6 (for an inhomogeneously broadened transition in an ensemble of two-level atoms) to analyze the dispersion of $\chi^{(3)}$ in the solutions studied here. In the model of Ref. 6, with $\nu_1 = \nu_m$, we find

$$|\chi^{(3)}| = K \left[\frac{(1 + R)^2 + \xi^2}{(1 + \Delta^2 T_1^2)(1 + \Delta^2 T_2^2)(1 + \xi^2)} \right]^{1/2}, \quad (1)$$

$$K = 2|\mu|^4 N_a \rho^{(0)} T_1 T_2 \hbar^{-3} / \Omega, \quad (2)$$

where $\Delta = 2\pi c(\Delta\nu)$, $\Omega = 2\pi cV$, $\xi = \Delta/\Omega$; $R^{-1} = T_2\Omega$; T_1 and T_2 are the energy and phase relaxation times, respectively, μ is the transition dipole moment, $\rho^{(0)}$ is the equilibrium population difference, and N_a is the concentration of aggregates.

A least-squares fit of Eq. (1) to the experimental data with $T_1 \approx 600$ ps (the measured duration of the fluorescence of the aggregates)¹⁾ yields $T_2 \approx 0.17$ ps. For solid (frozen) solutions of J aggregates of PIC, the value found for T_2 from photon-echo measurements⁸ decreases from tens of picoseconds to a few picoseconds as the temperature is raised over the interval 1.5–100 K. Comparing the results found here with the data of Ref. 8, we conclude that upon a further increase in the temperature, and a transition to the liquid state, the activation of dynamic electron–phonon interactions would reduce the time T_2 to subpicosecond values, and the exciton absorption band would broaden, remaining inhomogeneous ($R \approx 0.2$). Nevertheless, even for liquid solutions of J aggregates the value of T_2 is an order of magnitude higher than that for unaggregated molecules, because of the weakening of the coupling between electronic transitions and the motions of nuclei in the course of the aggregation.⁷

To estimate the absolute value $|\chi^{(3)}|$, we used the values of the intensity I_c at a detuning $\Delta\nu \approx 1 \text{ cm}^{-1}$ and at low values of I_1 and I_2 ($\leq 15 \text{ kW/cm}^2$), at which $|\chi^{(3)}(\Delta\nu \approx 1 \text{ cm}^{-1})|$ is independent of the pump power. According to these data, allowing for the absorption of all the fields, the value is $|\chi^{(3)}(\Delta\nu \approx 1 \text{ cm}^{-1})| \approx 10^{-7} \text{ cm}^3/\text{erg}$. The peak value of $|\chi^{(3)}|$, reached at $\Delta\nu = 0$, can be estimated from (1) to be $\sim 10^{-5} \text{ cm}^3/\text{erg}$. However, even the measured value $|\chi^{(3)}(\Delta\nu \approx 1 \text{ cm}^{-1})|$ is several orders of magnitude higher than the resonant cubic susceptibility of fast-response media (triphenylmethane dye solutions² and solutions of organic polymers⁹) and comparable to the susceptibility of semiconductor structures¹⁰ at a zero detuning!

Using the measured value of $|\chi^{(3)}|$, we can estimate the maximum absorption cross section σ_m and the concentration of aggregates. We can also estimate an upper limit on the number (n) of molecules in an aggregate. For the factor $|\mu|^4 N_a$ in (2) we find

$$|\mu|^4 N_a \approx \left(\frac{3hcV}{8\pi^3 \nu_m} \right)^2 \sigma_m \ln T^{-1} / l, \quad (3)$$

where T is the transmission of the solution. Substituting (3) into (2) and (1) with the

values found above for T_1 and T_2 and with the value $|\chi^{(3)}(\Delta\nu \approx 1 \text{ cm}^{-1})|$, we find $\sigma_m \approx 3.7 \times 10^{-15} \text{ cm}^2$ and $N_a \approx 2.8 \times 10^{17} \text{ cm}^{-3}$. Assuming that the aggregation in the solution is complete, we find $n \lesssim N/N_a \approx 6$. The estimates of σ_m and n found here on the basis of the four-wave mixing data are close to the values $\sigma_m \approx 2.3 \times 10^{-15} \text{ cm}^2$ and $n \approx 4$ found in Ref. 4 through a study of exciton annihilation in PIC solutions.

In conclusion we wish to stress that the parameters T_2 , σ_m , and n which we have been discussing here pertain to the "optical" aggregates which are responsible for the formation of the exciton band and the high optical nonlinearity of this medium. In contrast with "optical" aggregates, "chemical" aggregates can (according to Ref. 11) consist of tens of thousands of molecules, constituting a system of weakly bound "optical" aggregates capable of a mutual annihilation upon excitation.

¹We wish to thank T. V. Veselova for measuring T_1 .

²The comparison of the values of $|\chi^{(3)}|$ in solutions of J aggregates and in the solutions of the triphenylmethane dyes studied in Ref. 7 was carried out for a common optical density of the samples.

¹E. W. Knapp, Chem. Phys. **85**, 73 (1984).

²F. C. Spano and S. Mukamel, Phys. Rev. A **40**, 5783 (1989).

³E. E. Jelley, Nature **138**, 1009 (1936).

⁴H. Stiel *et al.*, Luminescence **39**, 351 (1988).

⁵Y. Wang, Chem. Phys. Lett. **126**, 209 (1986).

⁶T. Yajima and H. Souma, Phys. Rev. A **17**, 309 (1978).

⁷B. S. Neporent *et al.*, Opt. Spektrosk. **68**, 1285 (1990) [Opt. Spectrosc. (USSR) **68**, 755 (1990)].

⁸S. De Boer *et al.*, J. Chem. Phys. Lett. **137**, 99 (1987).

⁹B. P. Singh *et al.*, J. Chem. Phys. **92**, 2756 (1990).

¹⁰A. Krauze *et al.*, Opt. Spektrosk. **68**, 553 (1990) [Opt. Spectrosc. (USSR) **68**, 322 (1990)].

¹¹V. Sundstrom *et al.*, J. Chem. Phys. **89**, 2754 (1988).

Translated by D. Parsons