

rection of the entrance end of the cell. The maximum velocity of this motion is  $\sim 3 \times 10^9$  cm/sec. As the points move to the interior of the cell, their velocity decreases to approximately zero at the maximum of the laser pulse. The number of moving points is approximately equal to the number of self-focusing spots observed on the sweep of the exit end of the cell.

The photographs 2b and 2c show practically no backward motion of the self-focusing spots when the input-beam power is decreased. This can be attributed to violation of the self-focusing as a result of various energy-dissipation processes (for example, linear absorption), which are most appreciable precisely at the instant of reversal.

Under our experimental conditions, the maximum value is  $N = E/E_{cr} \approx 7$ , where  $E$  is the intensity of the input field,  $E_{cr} = [n_2(ka)^2]^{-1/2}$  ( $k$  - wave number,  $a$  - radius of entering beam,  $n_2$  - nonlinear refractive index). The theory developed in [3, 4, 15] predicts for  $N = 7$  and  $\zeta = \lambda/ka^2 \approx 0.5$  the existence of about 7 focal points, which is quite close to the experimental data obtained in our paper. The velocity of the focal points is also in satisfactory agreement with that calculated in [4].

The authors believe that the obtained experimental results confirm the validity of the self-focusing theory developed in [3, 4, 15].

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#### TWO-QUANTUM ANTI-STOKES PROCESSES IN THE EXCITATION OF DYES

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We report here an experimental observation of anti-Stokes Raman scattering by the electronic state of molecules and luminescence from the second excited electronic states in organic dyes.

In dyes used for saturable filters, luminescence in transitions from the second excited state to the ground state is quite easily observed, and its investigation is reported for example, in [1]. However, a more careful investigation of the spectra reveals, besides the

maxima of such a luminescence, also much weaker maxima coinciding in energy with the lines of the anti-Stokes Raman scattering on the first excited electronic state.

Several experimental investigations of the Stokes Raman scattering on the electronic states have by now already been reported. A review of these investigation is contained, for example in [2]. Anti-Stokes scattering was apparently observed only in [3], where previously excited  $\text{Cr}^{3+}$  ions in ruby were subjected to the action of neodymium-laser radiation of 1.06  $\mu$  wavelength. Insofar as we know, such processes were not observed previously in dyes at all, although from our point of view dyes are quite favorable research objects.

In our experiment, radiation from a pulsed ruby or neodymium-glass laser with peak power of about 50 MHz and pulse duration 20 nsec was incident on a cell with a dye solution of concentration on the order of  $10^{16} \text{ cm}^{-3}$ . The spectrum of the radiation scattered in the lateral direction was plotted point by point with the aid of a monochromator, a photomultiplier, and an oscilloscope. The laser pulse power was monitored with another photomultiplier.

An approximate scheme of the electron-vibrational bands of the dye, together with a designation of the considered processes, is shown in Fig. 1. The processes observed in our experiment are designated 7 and 8. It follows from the figure that to obtain anti-Stokes Raman scattering 8 it is necessary first to raise the atomic or molecular system to an excited state.

The anti-Stokes luminescence spectra obtained by us for three types of dyes are shown, corrected for the spectral sensitivity of the apparatus, in Fig. 2. In all the cases shown in this figure, the luminescence maximum corresponding to process 8 was observed on the short-wave slope of the maximum corresponding to the process 7, and its position coincided quite well with the sum of the energies of 3 and 4 of Fig. 1. Unfortunately, we were unable to measure the exact energy maximum of 3 in the case of polymethine dye, but as can be seen from Fig. 2a, the energy difference between the ruby and neodymium laser quanta, equal to  $5000 \text{ cm}^{-1}$ , agrees quite well with the energy difference of the corresponding 570 and 440 nm maxima. Additional proof of the process 8 proposed by us is also the fact that when the polymethine dye is excited by weak second-harmonic generation of wavelength 530 nm from the



Fig. 1. Energy-level and transition scheme: 1 - absorption of laser quantum, 2 - relaxation to lower states, 3 - single-quantum luminescence, 4 - absorption of laser quantum with transition to virtual level, 5 - relaxation to lower states, 6 - nonradiative relaxation to first excited state, 7 - luminescence from second excited state, 8 - anti-Stokes Raman scattering.

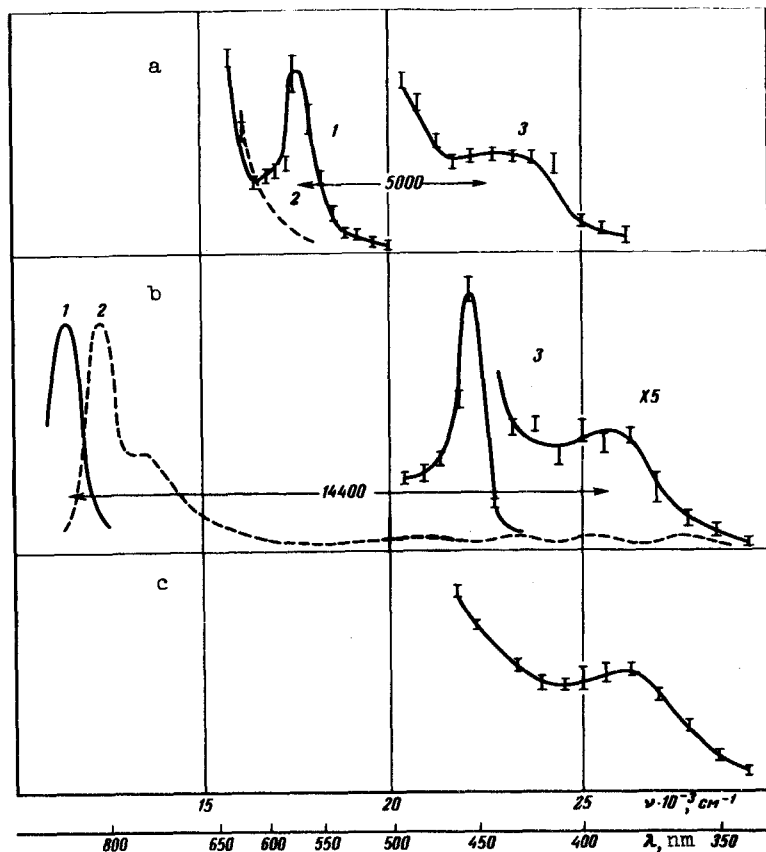


Fig. 2. Luminescence spectra: a - solution of polymethyl dye No. 7 from [5] in ethyl alcohol, maximum of absorption 1 near 1000 nm, maximum of process 3 - 1150 nm, maxima 1 and 3 corresponding to process 8 obtained by excitation at 1060 and 694 nm, curve 2 obtained by excitation at 350 nm directly from the ground state, arrows denote difference of the 1060 and 694 nm quantum energies in  $\text{cm}^{-1}$ ; b - solution of dye No. 10 from [5] in ethyl alcohol, curve 2 - absorption spectrum, curve 1 - single-quantum luminescence spectrum 3, curve 3 - excitation at 694 nm (scale of its right side magnified 5 times), arrows indicate excitation-quantum energy in  $\text{cm}^{-1}$ ; c - solution of phthalocyanine in toluol with excitation at 694 nm, maximum of absorption 1 near 694 nm, maximum of single-quantum luminescence 3 is at 740 nm.

ground state there is no maximum corresponding to the process 8, and only the process 7 is observed.

As shown by the theoretical estimates, when the transition 1 is saturated, the sought process 8 should be linear in terms of the power of the exciting laser radiation. Our experiments have shown that the intensities in all the maxima of the anti-Stokes luminescence observed by us, for both processes 8 and for processes 7, were linear in the excitation power within one or two orders of magnitude. A transition to a dependence steeper than linear was observed only when the power was insufficient to bleach the dye. The linearity indicates that the observed processes are not the result of two-photon excitation of the impurities, for otherwise the dependence on the power would be quadratic. The linearity of the process 7 following the saturation of transition 1 is obvious [1].

We measured also the polarization at different luminescence maxima, observed in a direction transverse to the exciting beam. In polymethine dye No. 7 excited by unpolarized radiation from a neodymium laser, the polarization ratio  $I_{\perp}/I_{\parallel}$  at the 570 nm maximum turned out to be  $0.74 \pm 0.12$ . For dye No. 10, this ratio, following excitation by polarized radiation from a ruby laser at the 380 and 450 nm maxima, equaled respectively  $0.63 \pm 0.05$  and  $0.50 \pm 0.06$ . It follows from the theory of Raman scattering that for transitions with a symmetrical polarizability tensor this ratio, obtained by excitation with polarized and unpolarized radiation, equals  $6/7$  and  $3/4$ , respectively. The experimentally obtained polari-

zation ratios for the process 7 are somewhat lower. They differ, however, in different maxima, thus indicating that they have a different nature. The lower polarization ratio can be attributed to the overlap of the spectra of processes 7 and 8. For process 7, the experimentally obtained polarization ratio does not contradict the theory if account is taken of the short lifetime in the excited state.

An absolute calibration of the apparatus sensitivity with the aid of a standard lamp has enabled us to measure the cross section of the process 8. It turned to be of the order of  $10^{-27} - 10^{-28} \text{ cm}^2$ . On the other hand, theoretical estimates of the cross section by means of the formula

$$\sigma \sim \frac{4\omega^2 d^4}{\hbar^2 c^4},$$

in which  $\omega$  is the average cyclic frequency of the transitions and  $d$  the dipole moment, give values from  $10^{-26}$  to  $10^{-29} \text{ cm}^2$ . A theoretical estimate of the cross section can also be obtained by determining  $d^4$  from the experimental results on two-photon absorption [4]. Such an estimate gives a cross section on the order of  $10^{-27} \text{ cm}^2$ , which agrees well with our data.

We must also point out some shortcomings of our interpretation. Thus, for example, all the short-wave maxima of the process 8 on Fig. 2 seem somewhat broader than the corresponding maxima of the one-quantum luminescence, and in the case of Fig. 2a the maximum 3 is even somewhat shifted towards the short-wave side. However, since these maxima overlap the maxima of processes 7, it is impossible to assess their actual width or exact position from the form of the curves of Fig. 2. A separation of the maxima is needed for this purpose. We indicate also that at the lifetimes characteristic of the processes in question, on the order of  $10^{-11} - 10^{-13}$  sec, the relaxation of 2 is apparently incomplete, and this also can cause broadening and a shift in the short-wave direction.

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#### GIANT FLUCTUATIONS OF PHOTOCURRENT IN GERMANIUM

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The phenomenon of exciton condensation in germanium was discussed in [1 - 6]. This effect consists of formation of metallized "drops" surrounded in the semiconductor by a dielectric gas of excitons. The presently available proof of the existence of such "drops" in pure germanium at helium temperatures and at a sufficiently high excitation level is based on data obtained only from purely optical experiments, and there is still no meeting of minds concerning the density and heat of sublimation of the condensate. Thus, the authors of [4, 5]