RESONANCE EFFECT OF LIGHT SCATTERING IN CRYPTOCYANINE

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We investigated the spectra of cryptocyanine vitrified in glycerine and crystallized in various matrices, viz., acetone, tetrahydrofuran, and dimethylformamide at various concentrations ($0.5 \times 10^{-4} - 10^{-6}$ mole/l). The solutions were frozen to 77°K. The beam of a ruby laser (20 MW) was sharply focused on the sample. The observation was from the side. The spectral instrument had a dispersion 12 cm^{-1}/mm.

The spectra of the samples revealed lines of various intensities (very narrow ones in crystalline samples), the analogs of which (with somewhat higher frequency) are seen in the infrared absorption spectra of cryptocyanine[1]. For example, the spectra of all samples are characterized by a doublet with frequencies 604 - 610 cm^{-1}, whereas the corresponding bands in the IR spectrum are 615 - 625 cm^{-1}. In addition, dye generation bands were observed, whose positions and character depended on the concentration of the substance. In each case, only lines falling in the generation band or situated in its immediate vicinity appeared. Typical spectra of the crystallized substance are shown in Fig. 1.

The fact that the lines are due to scattering and not to luminescence was demonstrated by the following experiments. The ruby-laser frequency was varied by changing the temperature. Under our conditions, the shift amounted to 4 cm^{-1}. The spectra pertaining to dif-
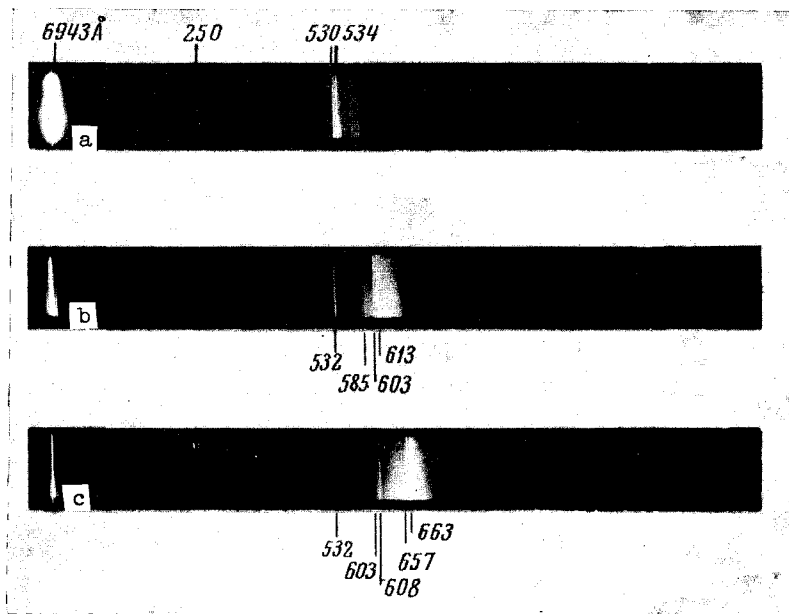

Fig. 1. Sections of spectra of crystallized cryptocyanine solutions in acetone (a), tetrahydrofuran (b) and dimethylformamide (c)

[1] The IR spectrum of cryptocyanine was obtained by using pellets with KBr in a Hilger H-800 instrument in the 400 - 2500 cm^{-1} range.

Fig. 2. Spectra of vitrified solution of cryptocyanine in glycerine following a 2 Å change of the exciting wavelength, demonstrating the shift of all the lines.

ferent positions of the exciting line were photographed one under the other on the same film in an immobile cassette. It turned out that all spectra shifted by 4 cm^{-1} (Fig. 2).

Control experiments were performed to determine the role of the generation band in the observed phenomena. In one case (vitrified substance) a third component, carbon bisulfide, was introduced into the system; its stimulated Raman scattering (SRS) line, 656 cm^{-1}, fell in the generation band. A comparison was made with a sample containing no cryptocyanine. No amplification of the SRS line of the carbon bisulfide was observed in this case. In other cases, a crystal matrix was prepared with two generating dyes, and the generation band of one of the dyes did not contribute to the appearance of SRS lines of the other. This proves, in our opinion, the absence of any effects of amplification by the excited dye molecules, similar to those observed in liquid systems in [1, 2].

On the basis of the foregoing, we intepret the spectra obtained by us as being due to resonant SRS proceeding not via the usual scheme ("from the bottom up"), but in accordance withe an "up" scheme through an intermediate virtual lower state allowed by the presence of inverted population. In the latter scheme, resonance sets in whenever the Stokes line of the Raman scattering falls in the luminescence region. We believe that this circumstance explains the connection established in our investigation between the occurrence of the spectral lines and the position of the generation band. It becomes clear, at the same time, that the process has a stimulated character, as is incidentally evidenced by the threshold conditions for its occurrence. Consequently, the observed lines should be attributed to vibrational transitions of the upper electronic state [3]. This is in good agreement with the aforementioned fact that the vibrational frequencies are somewhat lower in our spectra than in the IR spectra. The possibility of realizing in the scattering of a scheme of transitions "from the top down" and its peculiarities were taken into account by Placzek [4].

If the proposed mechanism is indeed responsible for the observed effect, then we can expect its manifestations also in Rayleigh scattering, particularly Stokes broadening of the SRS lines (but not of the laser line) as a result of their resonant Rayleigh scattering. Such a broadening (about 10 cm^{-1} was observed by us at a maximum spectrum excitation power (as expected, in the absence of laser-line broadening, for which the sharp-resonance conditios were not satisfied). It is therefore interpreted as resonant stimulated scattering of the line wing by cryptocyanine molecules excited by the electrons. The stimulated charac-
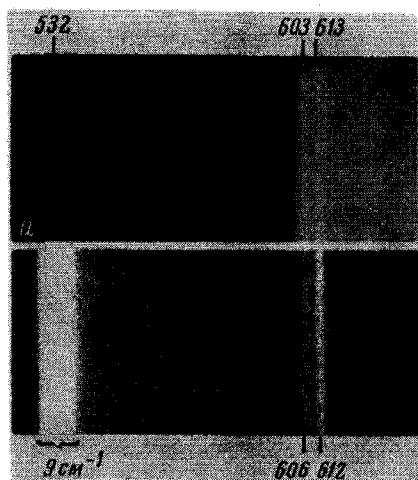

Fig. 1. Sections of spectra of crystallized cryptocyanine solution in tetrahydrofuran (a) and glycerine (b). Unilateral broadening of the line is seen in the latter case.

ter of the process is indicated by its distinct threshold observed by us. For ordinary Rayleigh scattering (and outside the resonance region), such an effect was first observed by Fabelinskii and co-workers in liquid substances [5] and was later investigated elsewhere. We propose that the line wing appears in our experiment as a result of rotational vibrations about the center of gravity of the molecules in solid vitrifying systems. A change of the polarizability anisotropy of anharmonic electronic oscillators under the influence of a powerful inhomogeneous field is perfectly possible [6]. Stokes broadening of SRS lines, which have the same nature, was recently observed by the authors of [7] in liquid substances, but with the spectra excited by picosecond pulses. Obviously, there should be no broadening of the line wing in crystallized matrices, in view of the fact that the molecules are rigidly secured. This was observed in experiment (Fig. 3), in full agreement with the expectations.

Thus, the following new phenomena were observed in the described experiments: resonant stimulated Raman scattering, and resonant stimulated Rayleigh scattering of the line wing in electron-excited states of molecules, realized via a nontrivial scheme of transitions "from the top down."

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POSSIBLE CASE OF VIOLATION OF THE INDEPENDENCE OF COMPOUND NUCLEUS DECAY OF THE INPUT CHANNEL SPIN

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Measurements of the angular distributions of reactions on nuclei with nonzero spin uncover new possibilities of verifying the independence of the compound-nucleus decay method of the input channel of the reaction.

Let us consider the case of a sell-insulated solitary resonance with angular momentum nad parity J^{π}, produced by interaction between a nucleon (it does not matter whether it is a proton or a neutron) with a target nucleus having a spin I. In this case the differential cross section of the reaction (a, b) is an incoherent mixture of two parts corresponding to two input channels with spins I - 1/2 and I + 1/2 [1].

The angular distribution of this reaction is given by the expression

$$W^{(b)}(\theta) \sim \frac{\Gamma_{a,\,I-1/2}\,\Gamma_b}{\Gamma^2} W^{(b)}_{J^{\pi},\,I-1/2}(\theta) + \frac{\Gamma_{a,\,I+1/2}\Gamma_b}{\Gamma^2} W^{(b)}_{I^{\pi},\,I+1/2}(\theta).$$