

RED AND BLUE FLUORESCENCE OF LASER-EXCITED CRYPTOCYANINE DYE SOLUTIONS

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Cryptocyanine is frequently used in laser technics as passive Q-switcher in impulse lasers and as active material of dye lasers. The mechanism underlying excitation and bleaching is not cleared up to this day. The aim of the authors is to prove that the investigation of the luminescence of cryptocyanine excited by a Q-switched rubin laser of variable intensity gives useful information about the electron transfer.

The authors studied the fluorescence and absorption spectra of cryptocyanine excited with the ground frequency and its second harmonics of a Q-switched laser and found that, in the case of high exciting intensities, luminescence in the blue range occurs instead of the red luminescence normally found. The blue luminescence is interpreted by a two-photon excited state and by photochemical reactions occurring in the excited state.

Introduction

Cryptocyanine is a dye frequently used in the field of lasers and laser spectroscopy, for instance as a saturable absorber for passive generation of nanosecond and picosecond ruby laser pulses, as active material of the dye laser and as a test molecule for new nonlinear optical devices. Hence it follows, that many informations on the cryptocyanine molecule were obtained. Nevertheless the basic mechanism of excitation and bleaching with ruby laser illumination is not yet fully explained. In this paper we try to show that the study of cryptocyanine luminescence by excitation with variable intensities of a Q-switched ruby laser gives useful informations on the electronic transitions involved in the saturation process and on photochemical reactions in several excited states.

Deactivation channels of the first excited singlet state S_{10}

At low excitation intensities only the normal red fluorescence of cryptocyanine can be observed. In Fig. 1 this radiative transition is indicated by a straight arrow between S_{10} and S_{00} . The quantum yield of the red fluorescence is $\eta = (7.5 \pm 2.0) \cdot 10^{-3}$ [1] resp. $\eta = (7.0 \pm 1.0) \cdot 10^{-3}$ [2] in ethanol and $\eta = (4.0 \pm 1.5) \cdot 10^{-3}$ in methanol [1].

Among the radiationless S_{10} -deactivations the ISC to the triplet is an unimportant process [2]¹, but the transition to a state S'_0 is an interesting channel. We interpret

¹ This and all the following results refer to alcoholic solutions.

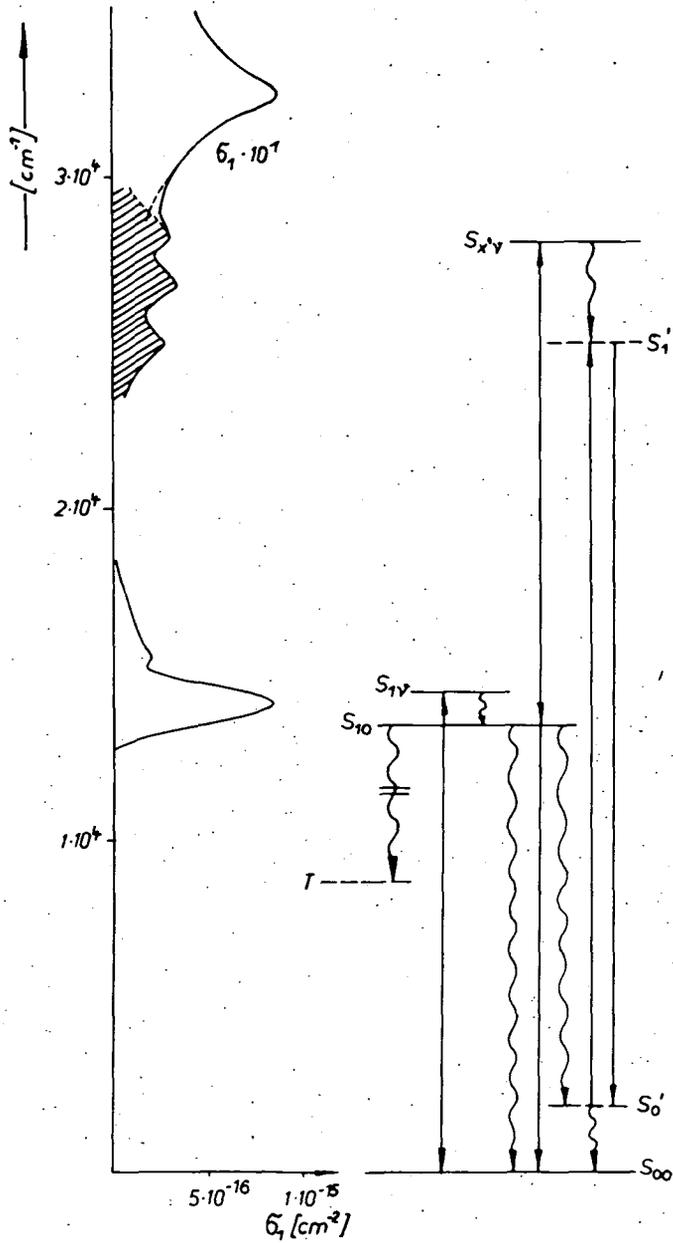


Fig. 1. Absorption spectrum of the ground state (on the left) and energy levels and transitions (on the right) of cryptocyanine in methanol. (The exact energetic position of the broken levels is unknown).

this state as the ground state of a fragment of the cryptocyanine π -electron system. We assume that the break is caused by interaction with a solvent molecule at positions of the cyanine chain with partial electron lack. Such interactions between cyanine dyes and solvent molecules of Lewis base type were studied by SCHEIBE *et. al.* [3] in the electronic ground state. In our case the break takes place in the first excited singlet state, the possible positions of a solvent attack are β , δ and the nitrogen atoms. (See Fig. 2.) For the identification of the photoproduct S'_0 there are at least three informations: The relaxation time of the S'_0 state is of the order of 200 nsec; the S'_0 absorption spectrum has a maximum at 430 nm [4-6]; the absorption maximum of a molecule like the terminal rings of cryptocyanine is located at 320 nm [7]. From absorption data we conclude that the break of the π -electron system of cryptocyanine by the transition $S_{10} \rightarrow S'_0$ takes place at the nitrogen atom. This is in accordance also with the absorption spectra of other fragments of the π -electron system of cryptocyanine, described below.

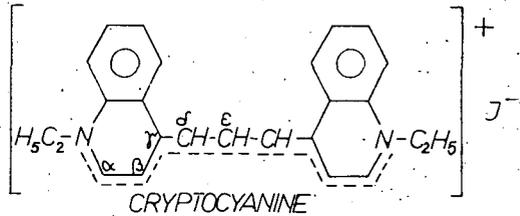


Fig. 2

Population and deactivation of higher excited states

Besides the normal red fluorescence, at sufficient ruby laser intensities we can observe a second fluorescence band, appearing in the blue range [4, 5]. The shape of the spectral band is shown in Fig. 3. The maximum is located at 462 nm, the half-width is about 50 nm.

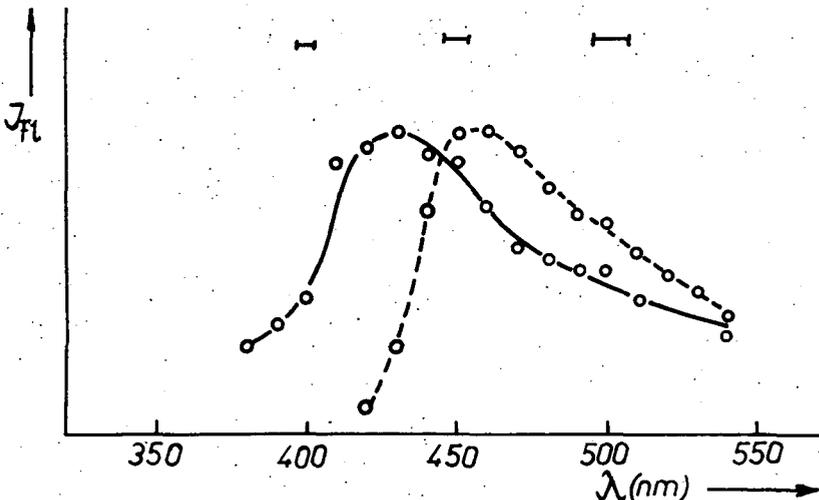


Fig. 3. Fluorescence spectra of a cryptocyanine/methanol-solution by excitation with a Q-switched ruby laser (broken line), or with its second harmonics (straight line).

This band indicates that a second absorption of a ruby photon takes place after the $S_0 \rightarrow S_1$ transition (see arrow between S_{10} and $S_{x'v}$ in Fig. 1). We have measured this excited state absorption band in the spectral range at 700 nm [8]; the maximum is located at about 710 nm with a maximum cross section $\sigma > 10^{-15} \text{ cm}^2$. According to our investigations described elsewhere [9], the terminal state of this S_1 -absorption is a two-electron excited state (a double excited configuration in the picture of simple one-electron orbital representation). The direct radiative combination of the state S_x with the ground state is forbidden. One of the deactivation channels of S_x is characterized by the blue fluorescence. The first

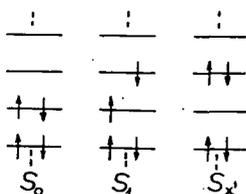


Fig. 4

step at this channel may be a radiationless transition to a one-electron excited state of corresponding energy. The vibrationless level of this state may be the starting level of the blue fluorescence. We assume, that this state is the first excited state S'_1 of the photoproduct of cryptocyanine mentioned above. There are two reasons for this assumption. First: The normal Stokes shift between the S'_0 absorption (430 nm) and the blue fluorescence. Secondly: The positions of the solvent attack in the cryptocyanine chain will be probably the same in the S_1 state and in the S_x state since the change in the electron density distribution at each atom of the cryptocyanine has the same direction for both transitions ($S_0 - S_1$, $S_1 - S_x$), caused by the identical orbital transitions. So we assume that the terminal state of the blue fluorescence is the S'_0 state.

Summarizing: The cycle $S_0 - S_1 - S_x - S'_1 - S'_0 - S_0$ represents one branch of the complex nonlinear absorption and deactivation of cryptocyanine at ruby laser irradiation.

Excitation with the second harmonic of a Q-switched ruby laser (347 nm)

In the case of 347 nm excitation we observe no red cryptocyanine fluorescence, but a fluorescence band at 430 nm (see Fig. 3.). An explanation of this result can be given on the basis of a new interpretation of the conventional cryptocyanine absorption spectrum. This points to the circumstance that the 3 bands between 350 and 400 nm (hatched part in Fig. 1) do not belong to the normal cryptocyanine molecule, but to similar fragments as discussed above in the case of the photoproduct. The positions of break of the π -electron system by solvent attack are now, in the ground state, the positions α or γ or ϵ . Consequently, irradiation of a cryptocyanine solution with the second harmonic of ruby produces excitation of such fragments. Therefore instead of the fluorescence of the normal cryptocyanine molecule, the blue fluorescence of fragments appears.

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КРАСНАЯ И ГОЛУБАЯ ЛЮМИНЕСЦЕНЦИЯ РАСТВОРОВ КРИПТОЦИАНИНА ПРИ ВОЗБУЖДЕНИИ ИЗЛУЧЕНИЕМ ЛАЗЕРА

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Криптоцианин как затвор для импульсных лазеров и активное вещество лазеров на красителях, широко используется в лазерной технике. Механизм возбуждения и просветления криптоцианина до сих пор не ясен. В работе показано, что исследование люминесценции криптоцианина при возбуждении моноимпульсным рубиновым лазером с разной интенсивностью дает полезную информацию об электронных переходах. Были исследованы спектры флюоресценции и поглощения при возбуждении основной и второй гармоникой моноимпульсного рубинового лазера. В случае интенсивного возбуждения вместе с красной люминесценцией появляется голубая люминесценция. Голубая люминесценция, по мнению авторов, объясняется как двухфотонным возбуждением, так и фотохимической реакцией в возбужденном состоянии.