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ON THE MECHANISM OF "HOLE BURNING" IN VIBRONIC SPECTRA
OF COMPLEX ORGANIC COMPOUNDS

Key words: photobleaching, hole burning

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The "hole burning" in continuous vibronic absorption spectra on photobleaching of dye solutions was usually investigated by two methods.

One set of experiments consists of direct measurements on light absorption by the cryptocyanine solutions irradiated by a Rb-laser monopulse ($\nu_b = 14400 \text{ cm}^{-1}$). From the measurements on absorption of photobleaching radiation of different spectral width ($\Delta\nu_{b_1} = 1, \Delta\nu_{b_2} = 0.05 \text{ cm}^{-1}$) Giuliano and Hess¹ found the width of a supposed "hole" to be $\delta\nu > 1 \text{ cm}^{-1}$. Using the flashlamp radiation for measurement of the absorption spectrum of the bleached solution Spaeth and Sooy² found that the width of a possible "hole" was $\delta\nu < 40 \text{ cm}^{-1}$ and that the solution did not undergo photobleaching outside the "hole" region. Contrary to these facts, it was shown in our experiments³ that the investigated solutions undergo nearly constant relative bleaching along their absorption spectra being measured by means of

radiation of a probe dye laser. In so doing, it was noted that an increase in transmission for bleaching radiation $\nu = \nu_b$ appeared to be more than that for measuring radiation of the broad-band probe dye-laser at $\nu_m = \nu_b$ (cf. Fig. 1). Bleaching of cryptocyanine solutions in a wide spectral region was also observed by Bonch-Bruevich, Razumova and Skorobogatov ⁴. Using a dye laser for measurements, they failed to observe any peculiarities in the absorption spectra of photobleached solutions. Lastly, Mourou, Drouin and Denariez-Roberge ⁵ directly observed the "hole" of the width $\delta\nu \approx 8 \text{ cm}^{-1}$ burned by a Rb-laser picosecond pulse. They used for the measurements a part of the same radiation, the spectrum of which had been broadened by means of self-phase modulation.

The contradictory results mentioned above are treated in different ways. The authors of Refs. ^{1,2,5} considered the formation of the "hole" as a "burning" of some components of inhomogeneously broadened vibronic spectrum of cryptocyanine. On the contrary, in Ref. ⁴ the ground electronic state of a cryptocyanine molecule is considered as homogeneously broadened one. Such broadening was ascribed in Ref. ² only to the absorption spectra of phthalocyanine solutions, since Gire ⁶ had observed no spectral "hole" when these solutions bleached. It should be noted that in our experiments ³ cryptocyanine and phthalocyanines displayed the similar properties of photobleaching.

In another set of experiments the spectral hole was investigated by means of forced synchronization of Rb-lasers

when a passively Q-switched slave laser was pumped by a monopulse of the master one, the former acting as the most sensitive indicator of the properties of the dye solution which forms the Q-switch. Opower and Kaiser⁷ bleached Q-switches (cryptocyanine solutions) of two slave lasers by one master pulse, forcing them to operate simultaneously and to capture the frequency ν_b of the master laser.

Soffer and McFarland⁸, using the metal-free phthalocyanine solution, and Hercher, Chu and Stockman⁹, using the solutions of phthalocyanines, also achieved pulse synchronization and frequency capture. These phenomena were observed in Ref.⁸ if the pulse delay of the slave laser did not exceed 400 μ sec. The pulse synchronization decreased this time to 50 nsec. The authors of Refs.^{8,9} considered the capture of the frequency ν_b by the slave laser with the formation of spectral "hole" on the background of the residual absorption of the Q-switch bleached by the master pulse. The formation of the "hole" in the Q-switch absorption spectrum had also been proposed by Röss¹⁰ and Soffer¹¹ in order to explain spectral narrowing of the Rb-laser with the formation of a giant pulse.

In the whole set of experiments^{7,8,9} the solutions of cryptocyanine and of the phthalocyanines behave in the same manner, that is in contradiction to the data and conclusions of Refs.^{2,6}. Moreover, our experiments showed that phthalocyanine solutions need an order factor lower powers of the master laser for synchronization and frequency capture.

At present there is no doubt that the bleaching of dye solutions in the limits of the whole vibronic absorption band is associated with decrease in the population of the levels of the initial ground state of molecules investigated under sufficient powerful radiation. (The distribution of molecules between the excited levels of the same (singlet) channel, the levels of isomeric configurations and states of other multiplicity (triplet ones) is the subject of calculation and investigation in a great number of papers).

In relation to the "hole burning" we are compelled to ascertain that the assumption of burning by means of bleaching radiation of the components of inhomogeneous broadening of the absorption spectra of the solutions under investigation cannot suggest an exhaustive explanation for the contradictory experimental data. In particular, transmission of photobleached solutions depends on the experimental conditions and on the properties of measuring radiation to a greater degree than on the type of absorbing molecules.

We are of the opinion, that distinguishing features of the absorption spectrum of photobleached solution which reveal as a "hole" near the bleaching radiation frequency ν_b must be associated with diffraction phenomena on labil (dynamic) holographic lattices. Such lattices are formed in the solutions under investigation as a result of optical transitions in the absorption centers in the interference field of bleaching and measuring beams. Depending on the following processes in the centers, the lattice may be amplitude or phase in character, but in all cases a part of

more powerful bleaching radiation diffracts on this lattice in the direction of the weaker measuring one. This diffraction effect gives rise to frequency capture in the experiments⁷⁻⁹ and is responsible for seeming decrease in the absorption near $\nu_m \approx \nu_b$ in the experiments⁵, in which the effective spectral width of the frequency ν_b is small enough to provide the formation of the lattice. An increase in the spectral width of ν_m involves a decrease in the lattice contrast and the widening of the diffracted beam, i.e. the disappearance of the "hole-burning" effect in the experiments²⁻⁴.

It is also likely that the elevated transparency of photobleached solutions for the bleaching radiation ν_b (Fig. 1) established in Ref.³ is caused by the formation of a system of standing waves when this radiation interferes with its part reflected from the walls of the cavity. In this case spatial redistribution of the light field intensity and nonlinear photobleaching of the solution in the regions of high field intensities result in an increase in the observed transparency of the structure in comparison to the solution influenced by travelling wave. The spectral-selective elevated transparency of the structure formed by standing waves in a passive Q-switch was applied by Schmackpfeffer and Weber¹² (contrary to Refs.^{10,11}) for explanation of the spectral narrowing of giant monopulses. Such a structure was observed in the experiments of Harrison, Key, Little, Magyar and Katzenstein¹³.

Based on the above considerations it is easily seen, that all results of interesting experiments of Derkacheva

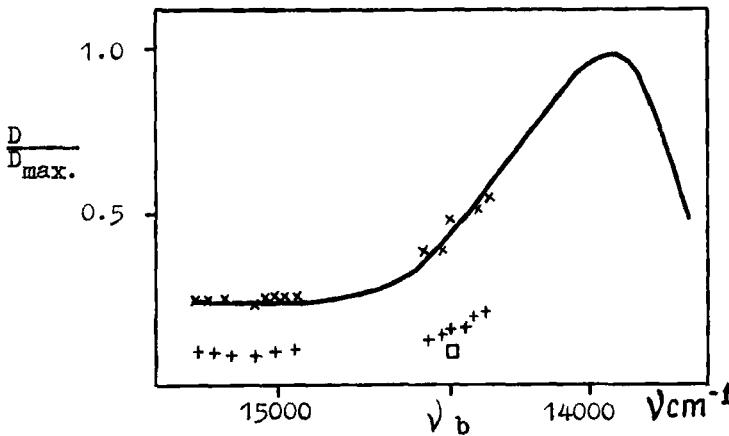


Fig. 1

The absorption spectrum of cryptocyanine in glycerol

- - of non-irradiated solution (measured by a spectrophotometer),
- xxx - of non-irradiated solution (measured by a probe organic dye laser),
- +++ - of photobleached solution (measured by a probe organic dye laser),
- - of photobleached solution (measured by photobleaching radiation itself).

and Petukhov¹⁴ can be explained by the action of the lattice formed in a dye solution by interaction of two exciting beams. Narrow band generation is explained by the selecting action of such a lattice, and the "generation" in the direction symmetrical to the cavity axis is explained by diffraction of this narrow band radiation at the lattice considered.

We succeeded to prove in the mentioned above experiments analogous to Refs. 7-9 that the frequency capture of the master laser by the slave one was precisely associated with

diffraction "injection" of a part of radiation of bleaching pulse b into the cavity of the slave laser by the above mechanism. We used the property of our master laser with active Q-switching to lase in some conditions two-frequency pulses (frequencies $\sqrt{b_1}$ and $\sqrt{b_2}$) with spacing 2.2 cm^{-1} when the width of each component was $= 0.04 \text{ cm}^{-1}$. It was established that if the passive Q-switched cryptocyanine slave laser was tuned to an intrinsic frequency $\sqrt{m} \approx \frac{\sqrt{b_1} + \sqrt{b_2}}{2}$ it captured both master laser frequencies on synchronization (Fig. 2), with lasing only these frequencies. Such a result would be impossible on burning of separate components in inhomogeneously broadened absorption spectrum of cryptocyanine, since according to reliable results of Refs^{1,5}, the hole width burned in this manner is about some more cm^{-1}

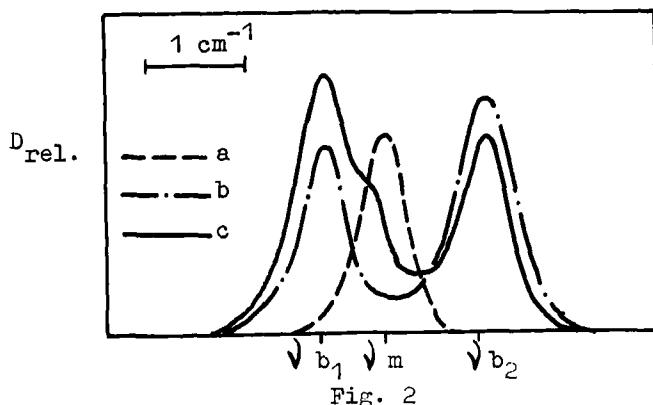


Fig. 2

Frequency capture

- a - the emission spectrum of the slave laser in a free regime
- b - the emission spectrum of the master laser
- c - the emission spectrum of the slave laser at frequency capture of the master one

which can provide no advantage of burning frequencies ν_{b_1} and ν_{b_2} compared to the intrinsic frequency ν_m . The diffraction "injection" makes this advantage to be possible.

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