Analysis of the parameters of Franck–Condon and Herzberg–Teller interactions the molecules of substituted diphenylbutadienes

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Abstract. We have done quantitative analysis of parameters Franck-Condon and Herzberg-Teller interactions of substituted diphenylbutadiene with general formula all-trans-X-Ph-$(C = C)_2$-Ph-Y (X, Y = H, NO_2, $N(CH_3)_2$, NH_2 various combinations). The research shows the influence of substituents on the vibronic parameters of characteristic bands, which describe the state (vibrations, types of deformation under excitation) of the phenyl ring and the polyene bridge at the diphenylbutadiene molecule. Results described impact of the substituent's nature on the parameters of intra- and intermolecular interactions presents for the studied compounds.

The methods of site-selective spectroscopy are very powerful for investigations of inter- and intra-molecular processes in complex organic dye doped solids (see e.g. [1-4] and references therein). In particular a lot of information about intramolecular interactions can be obtained by joint analysis of absorption and luminescence electronic-vibrational spectra of organic compounds. [5-8] In the majority works, which devoted to the spectra of substituted polyenes with trans-configuration, for the same substituted compounds there is considerable overlap between the general characteristic vibrational bands locations and these interpretations.

It is known that the substituents in the para position (in this study – nitro and amino groups) irrespective of their electronic nature violate uniform distribution of electron density in the molecule of DPB [9]. It should affect by the quantification of intramolecular interactions. Therefore, it was interest to produce comparative analysis of the spectral properties and quantification of the contribution of intramolecular interactions in the formation of the fine-structure spectra. The relative intensities of bands in the spectra of were calculated by the procedure described in [7, 8]. Based on the modern theory of molecular spectra in the adiabatic approximation ,which makes it possible to simultaneously take into account the influence of the Franck–Condon and Herzberg–Teller interactions on the shape of optical bands [10], we calculated the parameters a and α (of the FC and HT interactions, respectively) for each vibronic transition of the studied molecules.

In this study, the basic oscillations for substituted compounds were correlated with the interpretation of similar value 1,4-diphenylbutadiene, which spectral properties have been studied previously [11-13]. We shown to considered acceptors and donors, and besides the

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choice of the substituent in the aromatic ring was conditioned by the intention to show the obvious symmetry breaking, as well as variation for symmetry recovery.

The research showed that the parameters of intra- and intermolecular interactions, forming fine-spectra of the selected compounds exhibit a high degree of tolerance in the homologous row of molecules, and the possibility of a fragmented approach by the describing the fundamental bands. The obtained spectra confirm the validity of our findings, in addition the possibility of prediction them via vibronic parameters and select the type of substituent values - for the donor or acceptor interaction per molecule [12, 13].

It has been shown that the implantation of the diphenylpolyene's ring electron-donor or electron-acceptor substituent leads to broadening of the lines and increased background spectra. The implantation of substituents helps reduce the dipole moment of the molecule, which also reduces the value of the intermolecular interaction parameters. The comparative presence donor and acceptor in the different phenolic rings admitted to improves symmetry of the conjugate spectra, and significantly increase the internal energy of the molecule. Thus, the implantation of substituents does not affect to the localisation characteristic bands into the spectrum and can be used to strength the weak manifestation of the bands in the spectra of some luminophors.

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