THE NATURE OF $\pi$-ELECTRON TRANSITIONS IN THE SPECTRA OF 1-PHENYL POLYENES AND $\omega$-PHENYL POLYENALS

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On the basis of concepts with respect to the transitional matrix of the density, a new method has been proposed recently for analyzing the distribution of electron excitation over the fragments of a molecule [1]. In the present work this approach is used to solve the question of the relative contribution of "benzene" and "polyene" absorption to different $\pi$-electron transitions of 1-phenylpolyenes (PP) with different lengths of their polyene chain. The article discusses the spectra of para-$\hat{R}$-substituted PP, where $\hat{R}$ is a strong donor of the type of an amino group, and discusses the participation of the substituent in the overall molecular excitation. A comparison between calculated and experimental data is made also for the spectra of $\omega$-phenylpolyenals ($\omega$-PP) or iso-$\pi$-electronic PP corresponding to methyl ketones.

Method for Describing Electron Transitions

In experimental spectroscopy of complex conjugated molecules, long and fruitful use has been made of concepts of electron transitions, for which only individual parts (fragments) of a molecule are "responsible." Within the framework of the theory of MO (molecular orbitals), the local character of the electronic excitation is determined using configurational analysis, or from data on the change in the charge distribution in atoms with excitation. In [1] these approaches are examined critically and the following fact is pointed out: localization of the excitation in some fragment of the molecule means that the transition to an excited state takes place between natural orbitals localized in this fragment, i.e., orbitals diagonalizing the single-particle matrix of the density.

The quantitative criterion of the localization proposed in [1], directly reflecting the local nature of the natural orbitals, is based on a comparison between each atom $u$ and some...
Fig. 1. Types of transitions in the \( \pi \)-electron spectra of 1-phenylpolyenes \( \text{C}_6\text{H}_5-(\text{CH} = \text{CH})_n-\text{H} \). For a transition, the figure shows the degree of its localization in the benzene ring \( L_b \ (%) \) and the type of symmetry of the excited state for the linear configuration of the molecule; I, II, ... is the numeration of the types of transitions; \( \circ \) forbidden transitions with respect to their alternant character.

"localization number" \( L_{ij} \), which is a diagonal element of the square transitional matrix of the density \( \Xi \). The "measure" or "degree of localization" of the excitation in a fragment is introduced as the sum of all the localization numbers for the atoms of the given fragment: \( L_{f\Gamma} = \sum_{\text{at} \in \Gamma} L_{ij} \). The values of \( L_{f\Gamma} \) are always positive and vary from zero (the absence of excitation) to unity (complete localization of the excitation in the fragment).*

The matrix of the transitions \( D \) can be calculated on the basis of atomic orbitals, avoiding the construction of the matrix of the configurational interaction and the solution of the problem of eigenvalues [2]. When necessary, the \( D \) matrix can be constructed from the configurational coefficients \( \delta_{pi} \) and the coefficients with the \( \sigma_0 \) (atomic orbitals) in the corresponding occupied and vacant molecular orbitals

\[
D_{\mu\nu} = \frac{1}{\sqrt{2}} \sum_{\mu, \nu} (C_{\mu\mu}C_{\nu\nu} + C_{\mu\nu}C_{\nu\mu}) \delta_{pi}.
\]

*In the present article, the values of \( L_{f\Gamma} \) are given in percentages, and not in fractions of unity.