
FRAGMENTAL ANALYSIS OF ENERGIES OF ELECTRONIC TRANSITION IN MONOSUBSTITUTED
BENZENE DERIVATIVES. I. A SINGLE CONFIGURATION APPROXIMATION

K. V. Konstantinavichyus and V. M. Lazauskas

On the basis of the expression of the MO through fragment orbitals (FO) in monosubstituted benzene derivatives, the energies of the singlet electronic transitions in a single configuration (SC) approximation were decomposed into fragmental and interfragmental components. It was shown that the fragmental (phenyl) component is determined by the localization number (LN) of the MO and by transferable parameters—the corresponding values of SC transitions in benzene. As a result of changes in the LN in various molecules, both the fragmental (phenyl) component for various transitions and the interfragmental component change strongly. However, the expression of the MO through the FO makes it possible to carry out a sharp comparison of SC transitions in the parent (benzene) molecule and its substituted derivatives.

INTRODUCTION

The study of the regularities of the change in the electronic spectra of molecules during substitution is one of the main difficulties of the theory of spectra of molecules. The calculation method of the energies and the probabilities of the electronic transitions used at the present time (the PPP, CNDO/S, see [1-4]) give these characteristics for the molecule as a whole. Comparison of the electronic transitions in various molecules of the same class is usually carried out by comparing their energies and intensities according to the MO symmetry, etc. However, in this consideration it is difficult to reveal the structural factors determining these or other changes of the spectra of related molecules, since the LCAO MO are individual for each molecule. The localization of the MO in the chromophore group (fragment) is also different in different molecules, which still further complicates the comparison of the spectra.
On the other hand, the fragmental-stepwise diagonalization of the Fockian matrix makes it possible to obtain transferable fragment orbitals (FO) and their energy levels characteristic for a given fragment in various molecules. The uniqueness of the MO of the molecule is then determined by the difference in mixing of the FO. It should be noted that the LCFO MO is generally expressed through a smaller number of orbitals than in the case of LCAO MO. As a result, the analysis and the genealogical comparison of the MO of related molecules having a given fragment is substantially simplified.

Moreover, the expression of the MO through the FO naturally leads to a decomposition of the molecular values into fragmental and interfragmental components. The simplicity of the comparison of the LCFO MO of related (substituted) molecules substantially simplifies the analysis of the fragmental and interfragmental components and their changes, and the study of the relationship between the structure of the molecule (introduction of substituents) and its properties. On this basis, we shall examine the possibilities of fragmental analysis for studying the changes in the fragmental (mainly phenyl) and interfragmental components of the energies of long-wave electronic transitions in monosubstituted benzenes (MSB).

In the present work, we shall limit ourselves to an examination of the energies of singlet electronic transitions in a single configuration approximation (we shall use below the abbreviation - SC-transition) for the following MSB (see [8, 10]): aniline (An), orthogonal and planar phenol (Phn-o and Phn-p), benzoic acid (BA), nitrobenzene (NB) and styrene (St). For simplification of the analysis of the expressions of the energies of the electronic transitions (EET) we shall construct a model system of spectroscopic LCFO MO and their corresponding energy levels. We shall compare the calculated phenyl part of the SC transitions in the MSB with the value obtained by using the MO energies of benzene and also the coulombic and exchange integrals.

1. MODEL SYSTEM OF SPECTROSCOPIC MO OF MONOSUBSTITUTED BENZENES

The long-wave electronic transitions of benzene are transitions between the degenerated higher occupied $e_{1g}$ levels and the lower vacant $e_{2u}$ levels. Corresponding to these MO levels of benzene in the molecules of MSB are the FO of the phenyl fragment having a $B_2$, $A_2$ symmetry. For the sake of convenience, the FO of the phenyl fragment are designated as in [8], $\pi_s\pi_a$ from the $e_{1g}$ and $\pi_s^2\pi_a^2$ from the $e_{2u}$ level (here and below the indexes $s$ and $a$ denote symmetric and antisymmetric orbitals relative to a plane perpendicular to the plane of phenyl and passing through the rotation axis of the phenyl fragment). The energy levels (EL), the transitions between which determine the long-wave electronic spectra of the molecules and the corresponding MO, and also those MO which form FO, we shall call spectroscopic (SEL, SMO, SFO, respectively).

The formation of the MO in MSB was discussed in [10]. We shall briefly recall the formation of SMO corresponding to the higher occupied and lower vacant energy levels of the MSB studied. As shown in [10], the mixing of the FO during the formation of MO is determined by the difference of their energy levels and the value of the matrix element of the FO interaction. The latter in MSB differs substantially from the symmetrical $\pi_s$, $\pi_a$ and antisymmetrical $\pi_s^2$, $\pi_a^2$ FO of phenyl. For the $\pi_s$, $\pi_s^2$ FO of phenyl, it is equal or close to zero, and as a result, the $\pi_a$, $\pi_a^2$ FO of phenyl will mix very weakly with the FO of a substituting fragment (their weight in the MO does not exceed 1%), and therefore the FO of phenyl $\pi_a$, $\pi_a^2$ act practically as the MO in MSB.