Influence of intermolecular interactions on the electronic states and spectral and luminescent properties of bimolecular systems is analyzed. It is demonstrated that the spatial structure of single-electron states (molecular orbitals) must be analyzed in the initial stage of quantum-chemical study of this influence. The assumption that the overlap of molecular orbitals in contact complexes can be neglected is incorrect and leads to false conclusions about photophysics of such complexes.

Keywords: electronic states, photoprocesses, bimolecular systems, organic compounds.

INTRODUCTION

At the end of the 19th century, Wiedemann put forward a hypothesis about the decisive influence of the environment on the type of molecular luminescence. Analyzing experimental observations of luminescence, he assumed that a fluorescing body can be transformed into a phosphorescing one, limiting more and more the free mobility of its molecules (the Wiedemann dogma). And though later the Wiedemann conclusion was recognized to be incorrect, the great influence of the intermolecular interactions (IMI) on the spectral and luminescent characteristics of molecules caused no doubts and was the subject of numerous studies (for example, see [1, 2]). In molecular spectroscopy and luminescence, the universal (physical) IMI is manifested mainly through changes in the position, shape, and intensity of the emission and absorption bands. Specific (quasi-chemical) IMI can cause the occurrence (or vanishing) of new absorption and luminescence bands. Already in early stages of development of molecular luminescence, attention was focused on the problem of quenching of molecular emission, including quenching through incorporation of various impurities into the examined samples. These investigations culminated in the detection by Jean Perrin of the phenomenon of electronic excitation energy transfer (EEET) from one molecule (the donor D) to another molecule (the acceptor A).

H. Hellman [3] first applied quantum chemistry to investigate the EEET process. He determined wave functions, operators, resonance condition, and applicability limits for multipole expansion of the intermolecular interaction operator in a Taylor series. We note also that in [3] it was correctly emphasized that the theoretical interpretation of the phenomenon of nonradiative excitation energy transfer must be based on concepts of three branches of molecular physics, namely, quantum mechanics (quantum chemistry) of molecules, theory of intermolecular interactions of excited molecules, and theory of optical transitions. All these branches of molecular physics were intensively developed in the mid-thirties of the 20th century. This situation remained unchanged by the late forties when Förster formulated his theory. In the 50–60s, fast progress was observed and the basic laws were formulated in these branches of science (for example, in IMI spectroscopy [1, 2]). The possibility arose to check the concepts of the Förster theory based on new knowledge. However, by that time scientists had been under the firm
impression that the nonradiative EEET is a unique photoprocess (special type of deactivation of excited molecules), and only problems of relationships among the interaction matrix elements and energy difference between the initial and final states were discussed in studies devoted to the EEET theory.

We note that the role of the IMI in modern theory of nonradiative electronic transitions is also underestimated. Only nuclear (vibrational) coordinates of the medium are considered in the study of the system molecule-medium. The interaction with the electronic shell of the medium and its influence on the electronic states of the molecule are neglected. On the contrary, IMI spectroscopy is based on the assumption about the main role of this influence on the spectral characteristics of molecules in the condensed phase [1, 2]. In this case, other molecules of the same kind (concentration quenching), solvent, matrix, impurity, etc. can be considered as a medium.

Estimation of the rate constants of photoprocesses involves computation of the matrix elements of transition operators in terms of the wave functions of the initial and final electronic states. For many molecules in which the EEET process was experimentally investigated, fairly good results of computation of such wave functions were obtained already in the late fifties. However, despite the importance of estimation of the matrix elements [4], theoretical studies by the quantum-chemical methods were lacking.

Since the end of the 80s, we have been investigating theoretically the phenomenon of electronic excitation energy transfer in bichromophoric organic compounds and molecular systems (for example, see [5–10]). As a result of our studies, a quantum-chemical model has been constructed to study the orbital nature and spatial localization of electronic states and special features of the photoprocesses proceeding in such systems. It was established that the condition necessary for the occurrence of the intermolecular (inter-chromophoric) photoprocess is delocalization of the wave functions of electronic states participating in the photoprocess. This delocalization results from the intermolecular interaction between the system moieties (fragments). An analysis of the photophysical processes in such molecules and systems after photon absorption has demonstrated that the intermolecular nonradiative energy transfer proceeds via either internal conversion or intersystem crossing [6, 10]. Thus, it has been demonstrated that the origin of the intermolecular photoprocesses (including the type of the interaction initiating the electronic transition) does not differ from that of the intramolecular photoprocesses.

The intermolecular nonradiative electronic excitation energy transfer is only a special case of the influence of intermolecular interaction on the spectral and luminescent and photochemical properties of organic compounds. A correct description of mechanisms and relationships of intermolecular photoprocesses is required to investigate quenching of luminescence (including concentration quenching), complexes with charge transfer, and any arbitrary polymolecular systems.

In the present work, we discuss quantum-chemical aspect of spectroscopic IMI manifestations for bimolecular systems. The systems are investigated in which the complex is formed without specific interactions and local intermolecular chemical bonds (for example, hydrogen bond). Attention is focused on the wave functions of electronic states in such systems.

ELECTRONIC STATES OF BIMOLECULAR SYSTEMS

With allowance for intra- and intermolecular interactions, the total electronic Hamiltonian of the bimolecular system can be written in the form

\[ H = H_1 + H_2 + H_{12}, \]

where \( H_1 \) and \( H_2 \) are electronic Hamiltonians of the 1st and 2nd molecules:

\[ H_1 = \sum_{i} T_i + \sum_{i,k} \frac{1}{\varepsilon_{ik}} - \sum_{i,p} \frac{Z_p}{R_p}, \]