The influence of the photoinduced reversible intramolecular processes on the electron spin polarization.

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The report will summarize the theoretical results and the experimental observations of the dynamic equilibrium studied with the framework of a two-site model. The light absorption in molecular conjugates often produce the metastable excited states that are in the dynamic equilibrium. This situation arises during energy transfer between several chromophores, in metal-centered porphyrins (dynamic Jan-Teller effect), in proton exchange reactions, etc. Hopping between different local environments causes changes in the spectral and kinetic properties of the spin system, which can be studied by the electron paramagnetic resonance spectroscopy. Reversible transitions contribute to a number of phenomena some aspect of which have been investigated recently [1-4]. They include the repopulation of the spin polarized states; the developing of the net polarization; modification of the spectral shape function; enhancement of the flip-flop transitions induced by the remote weakly-coupled spins.

We have developed a two-site model which allows the characterization the reversible exciton hopping in the molecular conjugates. The key point of the two-site model is the existence of the common state $\rho = (k_B \rho_A + k_A \rho_B)/(k_A + k_B)$, which diagonal matrix elements repopulate relatively slowly while the remaining states rapidly depopulate during the reversible transitions. The rate constants, repopulating the spin sublevels i and j of the common state, equal:

$$K_{ij} = \frac{8 k_A k_B \left| (H_A - H_B)_{ij}/2 \right|^2}{(k_A + k_B)[(k_A + k_B)^2 + (H_A + H_B)_{ij}^2/4]}$$

Here, k_A and k_B are hopping rate constants, H_A and H_B are the spin-Hamiltonians of the sites A and B. These expressions provide simple relationship between the spectral and kinetic parameters of the excited molecules and allow analyzing the phenomena listed above.

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