Dynamic equilibrium in photoexcited molecular systems

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Light absorption in molecular systems often produces dynamic equilibrium between several excited states. In the case of photoexcited molecules, such states are metastable triplet states as well as charge-transfer states. Each of these states is characterized by its own set of the local interactions. For example, in molecular dyads composed of rigidly bound chromophore groups, these states are mainly determined by the parameters of the fine structure. In the case of dynamic equilibrium, transitions between different localized triplet states cause changes in the spectral and kinetic properties of the observed spin system, which can be studied using electron paramagnetic resonance spectroscopy.

We have recently proposed a two-site model that enables one to describe such phenomena [1-3]. One of the important concepts of this model is the existence of some common state $\rho = (k_B\rho_A + k_A\rho_B)/(k_A + k_B)$, which is characterized by the average spin-Hamiltonian H of the two triplet states. Here, k_A and k_B are the hopping rate constants. It was shown that due to reversible transitions, most of the matrix elements of the density matrix ρ can be neglected. To describe the observed phenomena it is enough to include only matrix elements that are diagonal in the basis of the eigenfunctions H. They are repopulated with the following rates:

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

Here, i and j are the indices of the spin sublevels, H_A and H_B are the spin-Hamiltonians of the sites A and B. The obtained expressions provide a simple relation between the spectral and kinetic parameters of excited molecules and enable the identification and study of excited states of molecules in dynamic equilibrium.

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