Dozy-chaos nature of molecular quantum transitions and theory of the optical band shapes in polymethine dyes

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Abstract

This work brings some completion to the theoretical explanation of a set of the optical band shapes in polymethine dyes, their dimers and aggregates. The explanation of all this remarkable diversity of optical bands, represented briefly in figure 1, is based on a new theory of elementary electronic charge transfers in condensed media, which has been developed by V.V.E. fairly fully, beginning with publications in 2001, and in their significantly approximate but still constructive manner, starting with publications in 1988 (although the first results were obtained as early as 1983 and were published in conference proceedings in 1985) (see [1] and the corresponding references therein). This theory is based on rejecting the famous and popular Franck–Condon views in the theory of the dynamics of molecular quantum transitions and replacing them with an understanding of the dynamics of the transient state of molecular quantum transitions, which has a chaotic nature (see [1] and references therein). Theoretical analysis of the dynamics of molecular transient states shows that in the process of a quantum transition the motions of electrons and nuclei are not much separated in time, as the Franck–Condon physical picture prescribes; on the contrary, they are aligned in time due to their joint chaotic motion. This chaos in the motion of electrons and nuclei exists only in the transient state and is absent from the initial and final states of molecular systems experiencing quantum transitions. It is therefore called dozy chaos. Introducing dozy chaos into molecular quantum mechanics has a forced nature and is associated with eliminating a substantial singularity in the probabilities (per unit time) of molecular quantum transitions (associated with the incommensurability of electron and nuclear masses), and it is the result of going beyond the adiabatic approximation. Considering a molecular quantum transition in the framework of the adiabatic approximation is tantamount to abandoning the dynamics of the transient state of a molecule, which in any case is always there. Formally, dozy chaos is introduced into the theory by replacing the infinitesimal imaginary addition in the energy denominator of the total Green's function of a molecular system with a finite value. This procedure was performed in its entirety in the simplest example of molecular quantum transitions taking the dynamics of the transient state into account, namely, in the example of elementary electron-charge transfers in condensed media. The simplicity is here associated with the opportunity to approximate the electron Green's function by a propagator and also with the opportunity to consider only non-local phonons and neglect local phonons. Because the main optical chromophore of polymethine dyes, the polymethine chain, has a quasi-linear structure with an alternating electronic charge along the chain, which is alternately redistributed on optical excitation, these dyes proved very convenient objects for numerous applications of the new theory of elementary electron-charge transfers. Thus, the theory of the optical band shape in polymethine dyes and their aggregates is not constructed as an *ad hoc* theory, as is often done by physicists or chemists (see [1] and the corresponding references therein), but is constructed as a by-product of the dozy-chaos theory of molecular quantum transitions. Theoretical atomic physics and theoretical nuclear physics were similarly constructed in the twentieth century, for example, as by-products of quantum mechanics.

The most basic results of the theory of the optical band shape in polymethine dyes and their aggregates (figure 1) are given and discussed in my recent paper [1]. The theory of the optical band shape based on dozy chaos and the corresponding calculation scheme for polymethine dyes and their aggregates can, of course, be generalized to a wide range of other objects studied in organic chemistry, but such a generalization, because of its grandeur, will undoubtedly require collective efforts of the scientific community. On the other hand, for confidence in the reliability of the new physical (dozy-chaos) picture of molecular quantum transitions and to control dozy chaos in the future, its direct detection of what V.V.E. said even earlier in 2013 (see [1] and references therein) is necessary. In this regard, experimentally studying the nuclear dynamics of the loss of regularity of a molecular structure in the chaotic transient state of molecular quantum transitions is one of the most important elements in studying the nature of dozy chaos. This kind of structural dynamics research using X-ray free electron lasers might be one of the key scientific developments in the near future.

Image

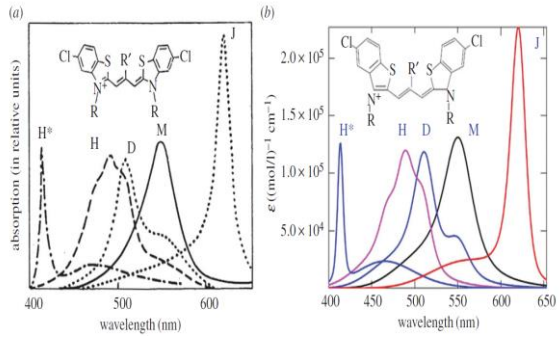

Figure.1: Theoretical optical absorption band shapes (b) in thia-polymethinecyanines [1] fitted to the basic experimental data (a) on polymethine dye monomers (M), dimers (D), H-, H*-, and J-aggregates.

Recent Publications

1. Nature of the optical band shapes in polymethine dyes and H-aggregates: dozy chaos and excitons. Comparison with dimers, H*- and J-aggregates, R Soc Open Science 4: 160550 (2017), Vladimir V. Egorov

2. Dozy-chaos end of the human civilization, J Ultra Scientist of Physical Sciences (B), 29 (4), 87-96 (2017), Vladimir V. Egorov

3. Nature of the narrow optical band in H*-aggregates: Dozy-chaos–exciton coupling, AIP Advances 4: 077111 (2014), Vladimir V. Egorov

4. Optical lineshapes for dimers of polymethine dyes: Dozy-chaos theory of quantum transitions and Frenkel exciton effect, RSC Advances 3(14): 4598 (2013), Vladimir V. Egorov

5. Dozy chaos in chemistry: Simplicity in complexity, in Chaos and Complex Systems, Berlin: Springer, 219-224 (2013), Vladimir V. Egorov

 **Biography**

Vladimir Valentinovich Egorov has his expertise in theoretical chemical physics. He has completed his PhD at the age of 32 years from Institute of Chemical Physics, USSR Academy of Sciences, and he has completed his Dr Phys&Math Sci degree (Electrodynamics of extended multiphonon transitions) at the age of 55 years from Institute of Physical Chemistry, Russian Academy of Sciences. He is leading research scientist at Photochemistry Center, Russian Academy of Sciences.

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