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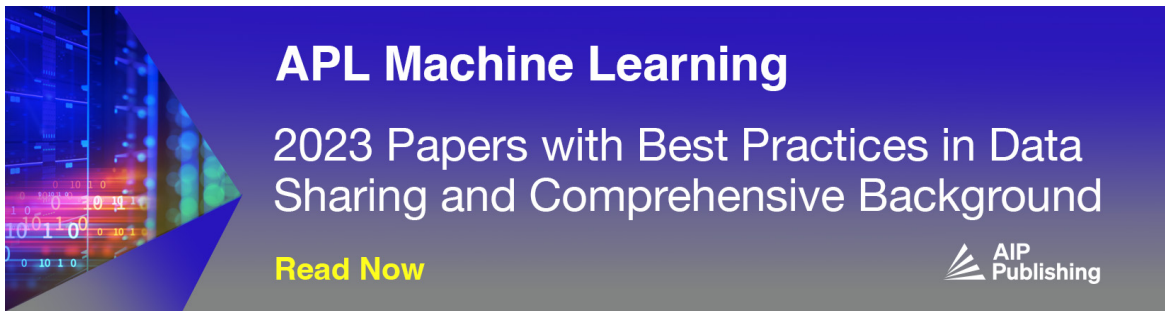
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## Nature of the narrow optical band in H<sup>\*</sup>-aggregates: Dozy-chaos–exciton coupling

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Dozy chaos emerges as a combined effect of the collective chaotic motion of electrons and nuclei, and their chaotic electromagnetic interactions in the transient state of molecules experiencing quantum transitions. Following earlier discussions of the well-known Brönsted relations for proton-transfer reactions; the temperature-dependent electron transfer in Langmuir–Blodgett films; the shape of the optical bands of polymethine dye monomers, their dimers, and J-aggregates, this paper reports one more application of the dozy-chaos theory of molecular quantum transitions. The qualitative and quantitative explanations for shape of a narrow and blue-shifted optical absorption band in H<sup>\*</sup>-aggregates is given on the basis of the dozy-chaos theory by taking into account the dozy-chaos–exciton coupling effect. It is emphasized that in the H<sup>\*</sup>-aggregate chromophore (dimer of cyclic bis-thiacarbocyanines) there is a competition between two Frenkel exciton transitions through the chaotic reorganization motion of nuclear environment. As a result, the highly organized quantum transition to the upper exciton state becomes an exciton-induced source of dozy chaos for the low organized transition to the lower exciton state. This manifests itself in appearing the narrow peak and broad wing in the optical spectrum pattern of H<sup>\*</sup>-aggregates. A similar enhancement in the H<sup>\*</sup>-effect caused by the strengthening of the exciton coupling in H<sup>\*</sup>-dimers, which could be achieved by synthesizing tertiary and quarternary thiacyanocyanine monomers, is predicted. © 2014 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License. [<http://dx.doi.org/10.1063/1.4889897>]

### I. INTRODUCTION

The interest in theoretical studies of the shape of optical bands for aggregates of polymethine dyes has awakened more than 70 years ago in connection with the discovery of the narrow and red-shifted J-band<sup>1</sup> (Fig. 1, left panel) in the experiments carried out by Jelley and Scheibe.<sup>2,3</sup> The theory and computer simulations of the shape of these optical bands have been particularly developed in the last 30 years. All the existing theoretical discussions of this problem were covered in our recent reviews.<sup>4,5</sup> There are two main and essentially distinct theoretical approaches to the problem: the author's one leaning upon the Green function method and so-called dozy chaos,<sup>4</sup> and the conventional concept based on the Born–Oppenheimer adiabatic approximation.<sup>6</sup> The former provides an explanation of optical spectra both for polymethine dye aggregates and for molecules composing them. The latter explains the optical spectra of dye aggregates but does not explain the spectra of constituent monomers.<sup>4,5</sup> What is more, the conventional approach does not explain experimental data on the optical band shape for H<sup>\*</sup>-aggregates. The purpose of this paper is to explain the nature of a narrow and blue-shifted optical absorption H<sup>\*</sup>-band (Fig. 1).

There are abundant experimental data on the shape of optical bands for polymethine dyes and their aggregates, which need, in general, a theoretical interpretation. However, the complete solution to this problem is very difficult. That is why, in the 70's of the last century, an experimental challenge

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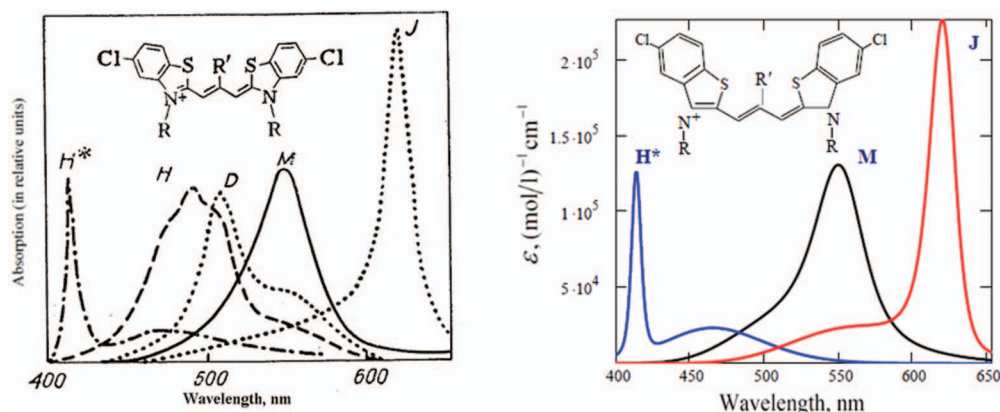


FIG. 1. Theoretical optical absorption band shapes for thiapolymethinecyanine (right panel) fitted to the available experimental data on dye monomers (M), J-, and H\*-aggregates ( $\epsilon$  is the extinction coefficient) shown in the general picture (left panel: D, dimers; H, H-aggregates) challenging in 1977.<sup>1</sup>

to the theory was formulated in the form of a single graph,<sup>1</sup> which depicts a typical shape of optical absorption bands for monomers, dimers, H-, H\*-, and J-aggregates. Figure 1 (left panel) presents all these typical experimental band shapes. It can be seen from this figure that the shape of the H\*-band resembles to some extent the shape of the dimer band: both bands give evidence of ‘blue’ peaks and ‘red’ wings. Therefore, it can be assumed that the main optical chromophore in H\*-aggregates constitutes a dimer. As is well known, exciton effects in the formation of a dimer optical band are rather important.<sup>4,5</sup> It will be explained below what are dozy chaos and dozy-chaos–exciton coupling.

## II. DOZY CHAOS AND DOZY-CHAOS–EXCITON COUPLING

The foundation of modern physics is laid by quantum theory which replaced the dominant position of classical physics about a hundred years ago with the introduction of Planck’s constant<sup>7</sup> and quantum jumps into physics. In those old times, one of the main problems in quantum theory was the explanation of the discreteness of optical spectra in atoms,<sup>8</sup> and quantum theory met this challenge brilliantly. The idea of quantum jumps or quantum transitions was completely alien to classical physics, but proved to be so fruitful in explaining a huge number of experimental evidences that it became generally accepted over time among the majority of physicists, despite the internal opposition to the quantum idea among some, even eminent physicists. Further scientific and technical progress was also associated with the subsequent development of quantum theory and the emergence of many its applications. In particular, theoretical molecular spectroscopy originated and flourished along with theoretical atomic spectroscopy. Advances of the former are based on the Born-Oppenheimer adiabatic approximation,<sup>6</sup> in which, to describe the collective motion of electrons and nuclei in molecules, a slow vibrational motion of nuclei is separated from the rapid motion of electrons. This approximation proved to be very fruitful for the theoretical description of the molecular structure and currently lies at the heart of modern quantum chemistry, solid state physics and many other physical and chemical disciplines. However, if we look at the dynamics of quantum transitions in molecules, here, in contrast to the atomic quantum transitions, the fundamental challenges of physical nature manifest themselves.<sup>9</sup> Namely, as is well known, a so-called reorganization of the nuclear subsystem takes place in the course of molecular quantum transitions, in which the equilibrium positions of the nuclei are forced to move so that their new position would be self-consistent with the new distribution of the electron charge density resulting from a quantum transition. The physical issue that arises here is how extremely light electrons manage to change the equilibrium positions of vibrating nuclei having huge masses and inertia for very short time of the quantum transition. These issues have no answer in the adiabatic theory, although this theory often gives results that agree well

with experimental data obtained in molecular spectroscopy. Thus, answers to the questions about the dynamics of molecular quantum transitions must be sought for beyond the adiabatic approximation.

From the formal point of view there is an essential singularity in the event of going far beyond the adiabatic approximation in considering the molecular quantum transition probabilities, which is a consequence of the incommensurability of the masses of electrons and nuclei involved in the transition. This singularity can be eliminated<sup>10–12</sup> by assuming that the electrons and nuclei are intensively exchanged by the kinds of motion and the amounts of energy during the quantum transition, the processes which are forbidden in the adiabatic approximation. These exchange processes lead to chaotization of the motion of electrons and nuclei in the transient state.<sup>4,5,13,14</sup> As a result of emerging this transient chaos, a part of the vibrational motion of the nuclei is transformed into the translational motion of their equilibrium positions to new positions in space, and then the translational motion transforms back to the vibrational motion near these new positions to complete the molecular quantum transition. Because this chaos arises only in the transient state and is absent in the initial and final states of the system, it may be called dozy chaos.<sup>4</sup> It should be noted that until recently<sup>4,5,9–14</sup> the modern physics and chemistry have been lacking for the idea of dozy chaos.

Dozy chaos emerges as a mix of the collective chaotic motion of electrons and nuclei, and their chaotic electromagnetic interactions (dozy-chaos radiation) in the transient state passed through during molecular quantum transitions.<sup>9,13,14</sup> Dozy chaos represents the universal physical phenomenon, universal to the same extent to which electrons and nuclei themselves are universal.<sup>9,13,14</sup> Dozy chaos provides the very possibility of quantum transitions and chemical reactions in general molecular systems.

Formally, dozy chaos is introduced into the dynamics of molecular quantum transitions through replacing the well-known infinitesimal imaginary addition  $i\gamma$  in the energy denominator of total Green's function of the system of electrons and nuclei by a finite quantity.<sup>4,5,9–14</sup> The value of  $\gamma$  can be imagined as the width of the vibronic energy levels arising in the transient state. However, a detailed and successful comparison of the theory with experiment<sup>4,5,10–15</sup> shows that the value of  $\gamma$  significantly exceeds the energy gap between vibrational levels. Therefore, the idea of  $\gamma$  as the width of vibronic energy levels in the transient state is very rough. In fact, such a large value of  $\gamma$  indicates that the exchange of the kinds of motion and amounts of energy between electrons and nuclei in the transient state is so intense that it leads to chaos (dozy chaos) in their motion. On the other hand, such a large value of  $\gamma$ , leading to dozy chaos, points to the continuity of the spectrum of vibronic energy in the transient state. In other words, a molecule, being a quantum system in the stationary state, for the time of a quantum transition becomes the classical one, which, as is well known, has a continuous energy spectrum.

It is remarkable that in the case of strong dozy chaos (the gamma value is of the order of reorganization energy of the nuclear subsystem  $E$  in a quantum transition or even larger:  $\gamma \geq E$ ), the results of the new theory based on Green's function method and dozy chaos phenomenon are consistent with the results of the standard theory based on the Born-Oppenheimer adiabatic approximation to a high degree of accuracy.<sup>4,5,11–14</sup> This is due to the fact that in the case of strong dozy chaos the probabilities (per unit time) of quantum transitions no longer depend on the chaotic dynamics of the transient state and depend only on the initial and final states. This fact is the reason why dozy chaos eluded researchers' attention for such a long time. Thus, under conditions of strong dozy chaos, which is often realized in practice, the standard theory of molecular quantum transitions gives correct results despite the fact that the latter results are obtained on the basis of erroneous physical concepts.<sup>4,5,11–14</sup>

In the case of very strong dozy chaos ( $\gamma \gg E$ ), the probabilities of quantum transitions are very small (in the classical language, we can speak about a very large internal friction in the system). The case of weak dozy chaos ( $\gamma \ll E$ ) corresponds to a high degree of the dynamic self-organization of molecular quantum transitions<sup>4,5,11–14</sup> and, consequently, to the large transition probabilities.

The new theory of molecular quantum transitions explains a great variety of experimental results,<sup>1–3,16–19</sup> which previously could not be interpreted correctly. These data include the shape of optical bands in polymethine dyes and their aggregates,<sup>1–5,10–15,17,18</sup> results in the well-known Brönsted relations for proton-transfer reactions,<sup>16,20</sup> and results for temperature-dependent electron

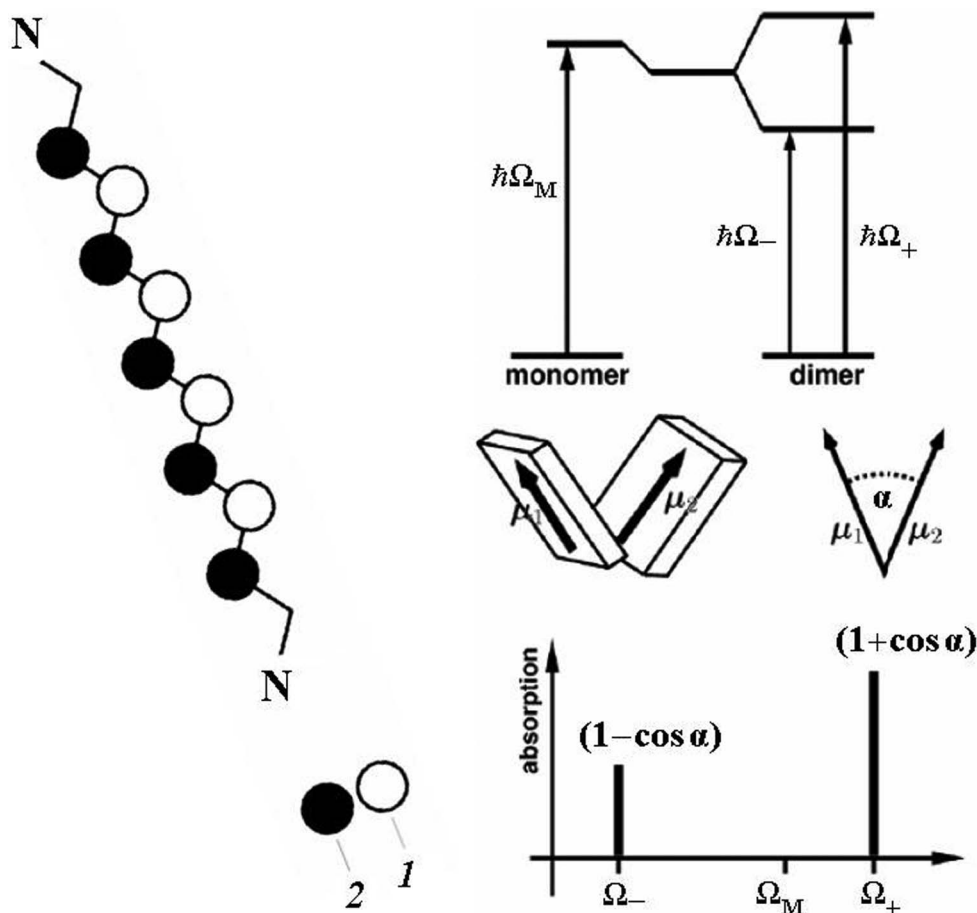


FIG. 2. Ideal polymethine state (left panel);<sup>22,23</sup> charges reside on carbon atoms of the polymethine chain in the ground state; charges: 1, positive; 2, negative. Excitonic shift and splitting in molecular dimers (right panel).<sup>24,25</sup> When the interaction of both the exciton transitions with the environment is absent, the optical absorption spectrum is given by two zero-width lines shifted relative to one another along the frequency axis (bottom right). ‘Switching on’ this interaction results in the transformation of both zero-width lines to optical bands of a nonzero width. On determining the interaction of electron (exciton) transitions with the motion of nuclei of the environment in the framework of the dozy-chaos theory of quantum transitions,<sup>13</sup> the optical band shape for the dimers of a polymethine dye is obtained.

transfers in Langmuir–Blodgett films.<sup>19,21</sup> The most striking examples of application of the new theory are provided by the shapes of narrow optical bands for J- and H\*-aggregates of polymethine dyes (Fig. 1). Quantum transitions in the main chromophore of their monomers, the quasi-linear polymethine chain (Fig. 2, left panel), can be considered approximately as extended quantum transitions in donor–acceptor systems embedded in condensed media (i.e., as elementary electron-charge transfers in condensed media).<sup>11,12</sup> The nature of the narrow and red-shifted J-band (Fig. 1) is explained by a good dynamic self-organization of the quantum transitions in the chromophore of J-aggregates (four molecules forming the structure of the brickwork type) for which the environmental nuclear dynamics in weak dozy chaos contributes to the electronic transition in the J-chromophore.<sup>4,5,10–12</sup> Exciton effects in the shape of the J-band are negligible. On the contrary, the nature of the narrow and blue-shifted H\*-band (Fig. 1) is explained by both the presence of dozy chaos and a sufficiently large exciton effect in a quantum transition and, moreover, by the strong interference interaction between them.<sup>15</sup> In the H\*-aggregate chromophore (dimer, Fig. 2) there is a competition between the two exciton transitions (Frenkel exciton)<sup>24,25</sup> through the chaotic reorganization motion of the nuclear environment. As a result, the more intense transition (to the upper exciton state) becomes well-organized, which shows itself as a narrow peak in the band shape, and vice versa, the less intense transition (to the lower exciton state) becomes more disorganized, which is exhibited by a

broad spectral wing. We call the discussed effect exciton–dozy-chaos interference effect,<sup>15</sup> or dozy-chaos–exciton interference effect, or dozy-chaos–exciton coupling effect. Formally, this dynamic interference effect is taken into account by considering the dependence of the dozy-chaos energy  $\gamma$  on the exciton states (see below).

### III. EXPLANATION FOR THE SHAPE OF AN H\*-BAND AND PREDICTION OF THE H\*-EFFECT GAIN

The dozy-chaos–exciton coupling equations for calculating optical absorption band shapes in dimers of polymethine dyes can be approximately given as follows:<sup>13</sup>

$$K_D = \frac{1}{2} [(1 + \cos \alpha) K_+(\Omega) + (1 - \cos \alpha) K_-(\Omega)], \quad (1)$$

where  $\alpha$  is the angle between the transition dipole moments of constituent molecules (Fig. 2);  $K_+(\Omega)$  and  $K_-(\Omega)$  are the rate constants for the transitions to the upper and lower exciton states, respectively. These are governed by the following equations

$$K = K_0 \exp W, \quad (2)$$

$$W = \frac{1}{2} \ln \left( \frac{\omega \tau \sinh \beta_T}{4\pi \cosh t} \right) - \frac{2}{\omega \tau} \left( \coth \beta_T - \frac{\cosh t}{\sinh \beta_T} \right),$$

$$+ (\beta_T - t) \frac{1}{\omega \tau \Theta} - \frac{\sinh \beta_T}{4\omega \tau \Theta^2 \cosh t}, \quad (3)$$

$$1 \ll \frac{1}{\omega \tau \Theta} \leq \frac{2 \cosh t}{\omega \tau \sinh \beta_T}, \quad (4)$$

where  $\beta_T \equiv \hbar \omega / 2k_B T$  ( $\omega$  is the phonon frequency), and

$$t = \frac{\omega \tau_e}{\theta} \left[ \frac{AC + BD}{A^2 + B^2} + \frac{2\Theta(\Theta - 1)}{(\Theta - 1)^2 + (\Theta/\theta_0)^2} + \frac{\theta_0^2}{\theta_0^2 + 1} \right], \quad (5)$$

$$|\theta_0| \gg \frac{E}{2J_1}, \quad (6)$$

$$\theta \equiv \frac{\tau_e}{\tau} = \frac{LE}{\hbar \sqrt{2J_1/m}}, \quad \Theta \equiv \frac{\tau'}{\tau} = \frac{E}{\Delta}, \quad \theta_0 \equiv \frac{\tau_0}{\tau} = \frac{E}{\gamma}, \quad (7)$$

$$\tau_e = \frac{L}{\sqrt{2J_1/m}}, \quad \tau = \frac{\hbar}{E}, \quad \tau' = \frac{\hbar}{\Delta}, \quad \tau_0 = \frac{\hbar}{\gamma} \quad (8)$$

Here, in turn, the following notation was used:

$$A = \cos \left( \frac{\theta}{\theta_0} \right) + \Lambda + \left( \frac{1}{\theta_0} \right)^2 N, \quad B = \sin \left( \frac{\theta}{\theta_0} \right) + \frac{1}{\theta_0} M \quad (9)$$

$$C = \theta \left[ \cos \left( \frac{\theta}{\theta_0} \right) - \frac{1 - \xi^2}{2\theta_0} \sin \left( \frac{\theta}{\theta_0} \right) \right] + M, \quad (10)$$

$$D = \theta \left[ \sin \left( \frac{\theta}{\theta_0} \right) + \frac{1 - \xi^2}{2\theta_0} \cos \left( \frac{\theta}{\theta_0} \right) \right] - \frac{2}{\theta_0} N, \quad (11)$$

$$\xi \equiv \left(1 - \frac{E}{J_1}\right)^{1/2} \quad (J_1 > E \text{ by definition}), \quad (12)$$

and where, finally, one has

$$\Lambda = -(\Theta - 1)^2 E + \left[ \frac{(\Theta - 1)\theta}{\rho} + \Theta(\Theta - 2) \right] E^{\frac{1-\rho}{1-\xi}}, \quad (13)$$

$$M = 2\Theta(\Theta - 1)E - \left[ \frac{(2\Theta - 1)\theta}{\rho} + 2\Theta(\Theta - 1) \right] E^{\frac{1-\rho}{1-\xi}}, \quad (14)$$

$$N = \Theta \left[ \Theta E - \left( \frac{\theta}{\rho} + \Theta \right) E^{\frac{1-\rho}{1-\xi}} \right], \quad (15)$$

$$E \equiv \exp\left(\frac{2\theta}{1+\xi}\right), \quad \rho \equiv \sqrt{\xi^2 + \frac{1-\xi^2}{\Theta}}. \quad (16)$$

Factor  $K_0$  takes the form

$$K_0 = K_0^e K_0^p, \quad (17)$$

where

$$K_0^e = \frac{2\tau^3 J_1}{m} \frac{(A^2 + B^2) \rho^3 \Theta^4 \xi}{\theta^2 \left[ (\Theta - 1)^2 + \left( \frac{\Theta}{\theta_0} \right)^2 \right]^2 \left[ 1 + \left( \frac{1}{\theta_0} \right)^2 \right]} \quad (18)$$

and

$$K_0^p = \frac{1}{\omega\tau} \left[ 1 + \frac{\sinh(\beta_T - 2t)}{\sinh \beta_T} \right]^2 + \frac{\cosh(\beta_T - 2t)}{\sinh \beta_T}. \quad (19)$$

In Eqs (7) and (8),  $J_1$  is the electron binding energy in the initial state 1,  $m$  is the effective mass of electron,  $L$  is the polymethine chain length, and  $\Delta$  defines the thermal effect energy related to heat absorption (or heat release) in elementary electron-transfer processes (extended quantum transitions or extended multiphonon transitions). The energy  $\hbar\Omega$  of the absorbed photon and thermal effect  $\Delta$  are related by the law of conservation of energy:

$$\hbar\Omega = J_1 - J_2 + \Delta, \quad (20)$$

where  $J_2$  is the electron binding energy in the final state. The time scales given by Eq. (8) control the dynamics of extended quantum transitions. They are discussed in detail in Refs 4,5,12, and 26.

The quantity  $K = K(\Theta, \theta_0)$  and the corresponding optical extinction coefficient  $\varepsilon$  are related as follows

$$\varepsilon = \frac{4\pi^2 q^2 N_A \Omega}{3\hbar c n_{\text{ref}}} K, \quad (21)$$

where  $q$  is the amount of electron charge transferred in an extended multiphonon transition,  $c$  and  $n_{\text{ref}}$  are the speed of light in vacuum and the refractive index, respectively, and  $N_A$  is the Avogadro constant.

The results of the theoretical fitting of the optical absorption band shapes for monomers and dimers to the experimental data<sup>1</sup> are given in Ref. 13 and they are plotted in Fig. 3 (cf. Fig. 1, left panel).

The results of the theoretical fitting of the optical absorption band shape for H<sup>\*</sup>-aggregates to the experimental data<sup>1</sup> are shown in Fig. 3 and Fig. 1 (right panel). As can be seen from Fig. 3 [Fig. 1 (right panel)] and Fig. 1 (left panel) there is a good agreement between theory and experiment. It was found that the dozy-chaos energy  $\gamma$  for the upper exciton state is much less (by an order of magnitude) than that for the lower exciton state (Fig. 3, caption; cf.  $\gamma^+ = 0.09$  eV and  $\gamma^- = 1.16$  eV). This corresponds to a high organization of the quantum transition to the upper exciton state (the

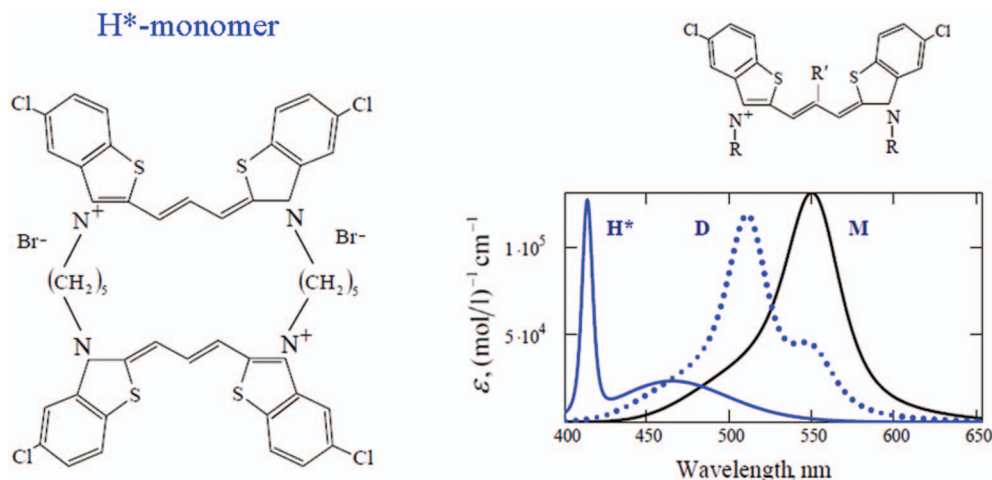


FIG. 3. Theoretical optical absorption band shapes of thiapolymethinecyanines fitted to the available experimental data on polymethine dye monomers (M), dimers (D), and H\*-aggregates (wavelength  $\lambda = 2\pi c/\Omega n_{\text{ref}}$ ) shown in the general picture challenging in 1977 (see Fig. 1, left panel). The polymethine chain length  $L = 6d$ , where  $d$  stand for certain, roughly equal bond lengths in the chain. The absorption bands are computed from Eqs (1)–(21) when fitting them to the experimental data in terms of the wavelength  $\lambda_{\text{max}}$ , extinction coefficient  $\varepsilon_{\text{max}}$ , and half-width  $w_{1/2}$  with a high degree of accuracy. The following parameters of the ‘dimer + environment’ system are utilized:<sup>13</sup>  $\alpha \equiv \alpha(\text{D}) = 61^\circ$ ,  $q \equiv q(\text{D}) = 1.4e$ , where  $e$  is the electron charge;  $m = 3.5m_e$ ,  $\omega = 5 \times 10^{13} \text{ s}^{-1}$ ,  $d = 0.14 \text{ nm}$ ,  $n_{\text{ref}} = 1.33$ ,  $J_1 = 5.4 \text{ eV}$ ,  $J_1 - J_2^- = 1.43 \text{ eV}$ ,  $J_1 - J_2^+ = 1.56 \text{ eV}$ , hence excitonic splitting energy  $J_2^- - J_2^+ \equiv \Delta J(\text{D}) = 0.13 \text{ eV}$ ,  $E = 0.21 \text{ eV}$ ,  $\gamma = 0.15 \text{ eV}$ , and  $T = 298 \text{ K}$ . The following parameters of the ‘H\*-aggregate + environment’ system are involved:  $\alpha \equiv \alpha(\text{H}^*) = 70^\circ$ ,  $q \equiv q(\text{H}^*) = 2.26e$ ,  $m = 3.5m_e$ ,  $\omega = 5 \times 10^{13} \text{ s}^{-1}$ ,  $d = 0.14 \text{ nm}$ ,  $n_{\text{ref}} = 1.33$ ,  $J_1 = 5.4 \text{ eV}$ ,  $J_1 - J_2^- = 1.67 \text{ eV}$ ,  $J_1 - J_2^+ = 2.11 \text{ eV}$ , excitonic splitting energy  $J_2^- - J_2^+ \equiv \Delta J(\text{H}^*) = 0.44 \text{ eV}$ ,  $E^- = 0.2 \text{ eV}$ ,  $E^+ = 0.1 \text{ eV}$ ,  $\gamma^- = 1.16 \text{ eV}$ ,  $\gamma^+ = 0.09 \text{ eV}$ , and  $T = 298 \text{ K}$ .

narrow ‘blue’ peak in the H\*-band) and a low organization of the transition to the lower exciton state (the broad ‘red’ wing) as mentioned above (see Section II).

It is of common knowledge that the H\*-band is shown by polymethine dyes having a specific structure. Namely, H\*-aggregates are generated by cyclic bis-thiacarbocyanines, i.e., by two similar polymethine dye monomers lying approximately in the same plane, whose polymethine chains are cross-linked to each other at their ends by hydrocarbon radicals (Fig. 3, left panel).<sup>18</sup> This linkage approximately results in doubling of transition dipole moments (Fig. 3, caption; cf. charges  $q(\text{D}) = 1.4e$  and  $q(\text{H}^*) = 2.26e$ ), due to which the dye monomers are excitonically coupled in the chromophore dimers in H\*-aggregates, and this, in turn, results in quadrupling (with the same geometry of the ordinary dimers and H\*-dimers) of the excitonic splitting energy (Fig. 3, caption; cf.  $\Delta J(\text{D}) = 0.13 \text{ eV}$  and  $\Delta J(\text{H}^*) = 0.44 \text{ eV}$ ,  $\alpha(\text{D}) = 61^\circ$  and  $\alpha(\text{H}^*) = 70^\circ$ ). Such a significant increase in the exciton interaction is the cause of the above competition between exciton transitions, which explains the nature of the H\*-band.

Note that the fitting exhibits not only the above-mentioned strong dependence of dozy-chaos energy  $\gamma$  on exciton states, but also a weak dependence of reorganization energy  $E$  on these states: the value of  $E$  for the upper exciton state is slightly less (half as much) than that for the lower exciton state (Fig. 3, caption; cf.  $E^+ = 0.1 \text{ eV}$  and  $E^- = 0.2 \text{ eV}$ ). This fact is explained by the large excitonic splitting obtained above by fitting for cyclic bis-thiacarbocyanines. Such a large excitonic splitting results in the electron density distribution that is much less compact in the upper exciton state than in the lower one. This more diffuse distribution, in its turn, gives rise to weaker electron–phonon coupling and, hence, to smaller reorganization energy  $E$ .

It should also be noted that the dozy-chaos–exciton interference effect can be considered as ‘a process’ in which the low organized quantum transitions (to the lower exciton state) pump out dozy chaos from the highly organized transitions (to the upper exciton state) by the Frenkel exciton movements. In other words, the highly organized quantum transition is the exciton-induced source of dozy chaos for the lowly organized transition.



In conclusion, it is worth drawing attention once again to the fact that the self-organization of quantum transitions, which results in the narrow H\*-band, differs radically in nature from the self-organization resulting in the narrow J-band. In the case of the J-band<sup>4,5,10-12</sup> there is a high degree of self-organization in the transient state, in which the ordered component of chaotic motion of the nuclear subsystem contributes to the electronic transition in the J-chromophore. In this case, the ‘imaginary’ (dynamic) part of a ‘complex reorganization energy’<sup>13,15</sup> of the nuclear subsystem is typically much smaller than its ‘real’ (static) part:  $\gamma \ll E$ .<sup>4,5,10-12</sup> In the case of the H\*-band, a more chaotic (as compared with the case of the J-band) motion of the nuclear subsystem in the transient state sets up a barrier to the quantum transition, and the self-organization of its transient state is associated with a competitive repartition of chaos (dozy chaos) between two exciton states due to increased exciton interaction. In this case, for the peak of the H\*-band, the dynamic part of the ‘complex reorganization energy’ is on the order of magnitude of its static part, and for the wing — a lot more about:  $\gamma^+ \cong E^+$  and  $\gamma^- \gg E^-$  (Fig. 3, caption; cf.  $\gamma^+ = 0.09$  eV and  $E^+ = 0.1$  eV,  $\gamma^- = 1.16$  eV and  $E^- = 0.2$  eV). In simple terms, the low barrier in the quantum transitions determining the shape of the peak in the H\*-band is caused by the high barrier in the quantum transitions determining the band shape of its wing.

The optical H\*-effect could be intensified by using larger planar monomers in chromophore dimers forming H\*-aggregates. For a given geometry of the H\*-dimer, adding another identical polymethine chain to the H\*-monomer (Fig. 3, left panel) parallel to the two existing ones (tertiary thiocarbocyanines) would enhance the excitonic splitting energy and the corresponding  $\Omega$ -distance between the peak of the H\*-band and the top of its wing by a factor of about  $9/4$ , while adding one more polymethine chain (quarternary thiocarbocyanines), by a factor of about  $16/9$ . This strengthening of the exciton coupling in the H\*-chromophores would result in the enhancement of the interference interaction between dozy chaos and excitons and, hence, in a sharper peak in the H\*-band. Such larger planar monomers, tertiary and quarternary thiocarbocyanines, have not been found so far. Therefore, the synthesis of like monomers seems to be rather promising for future applications.

#### IV. SUMMARY

In addition to a number of applications mentioned in Section II and demonstrated earlier (the well-known Brönsted relations for proton-transfer reactions,<sup>20</sup> the temperature-dependent electron transfers in Langmuir–Blodgett films,<sup>21</sup> the shape of the optical bands of polymethine dye monomers<sup>12</sup> and their dimers<sup>13</sup> and J-aggregates),<sup>10-12</sup> the theory outlined implies another application of the dozy-chaos concept of molecular quantum transitions. In this article, the qualitative and quantitative explanations of the shape of the narrow and blue-shifted optical absorption band in H\*-aggregates are given based on dozy-chaos theory with regard to the dozy-chaos–exciton coupling effect. Namely, in the H\*-aggregate chromophore (dimer) there is a competition between two Frenkel exciton transitions due to the chaotic reorganization motion of the nuclear environment. As a result, the highly organized quantum transition to the upper exciton state becomes the exciton-induced source of dozy chaos for the lowly organized transition to the lower exciton state. This shows itself as a narrow peak and a broad wing in the optical band shape of H\*-aggregates. It is predicted that the H\*-effect might be enhanced by strengthening the exciton coupling in H\*-dimers using tertiary and quarternary thiocarbocyanine monomers.

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