PHOTO-INDUCED MULTIELECTRON TRANSFER IN ORGANIC CRYSTALS WITH MIXED-STACK ARCHITECTURE.

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Abstract.

We discuss the photo-induced multielectron transfer in organic mixed-stack charge-transfer crystals, close to the neutral-ionic interface. The quasi-one-dimensional architecture of the stacks stimulates intermolecular electron transfer and the energy gain due to Coulomb interaction creates highly cooperative electronic excitations, the charge-transfer strings. At the neutral-ionic interface charge-transfer exciton is no longer elementary excitation and a pair of neutral-ionic domain walls plays such a role. Photo-generated strings proliferates as a motion of lattice-relaxed neutral-ionic domain walls, a «domino effect» caused by electron-phonon coupling. We show that the cooperative multielectron transfer in tetrathiafulvalene-chloranil (TTF-CA) crystal can be photo-induced as bidirectional transition between neutral and ionic phases. Apart from many application-oriented aspects, the discussed phenomena, photo-induced cooperative multielectron transfer, may serve as a model for the electron-transfer self-organization, the frontier problem in natural sciences.

1. Introduction.

It is well known that an electron in an insulating condensed environment induces a local reorganization when excited by a photon. The phenomena are called an electron solvation in a liquid or lattice relaxation of an optical excitation in a solid. It has been considered as a very local concept and the environment treated as a passive bath. Recent years have shown that there are many unconventionally photoactive condensed phases, where the relaxation of an excited electron results in various cooperative phenomena. This involves large number of atoms and electrons, indicating that an environment plays important and active role. These cooperative phenomena seem to mimic what the nature has developed to a high degree of perfection: the self-organization. For solids it is suggested to call the phenomena «photo-induced structural phase transition» (PIPT) [1].

Among all, the electron transfer processes are extremely important as they are at origin of mechanisms of processes, from biology to (heavy) industry. In a passive medium, an electron transfer is driven by the medium fluctuations as described by Marcus' theory [2]. When an electron transfer is accompanied by a chemical bonding, the medium is strongly (chemically) reorganized and the process is called passive self-organization. In case of interfacial reaction, the chemical binding of an electron helps to achieve favorable electrochemical potential for the electron transfer [3]. The «photon driven proton pump» in liposome bilayer, on the other hand, is the spectacular example where electrical potential derived from photo-induced electron transfer in porphyrin moiety leads to directional proton transfer [4,5]. The efficient long-distance electron transfer mediated by hydrogen bonds is another fascinating example [6]. In the passive self-organization, the electron transfer process is coupled to a chemical reaction, with a direct conversion of electrical and chemical potentials. However, according to ref. [3], a simple observation that an electron transfer processes in chemical industry require high temperatures («hard chemistry») while corresponding processes in living systems are efficient at environmental conditions, strongly suggests that the processes in nature are multielectron transfer. They are governed by dynamic self-organization, which involves an active medium. In such a process, a medium is required to supply some amount of energy to accelerate the electron transfer and causes cooperativity of the process. The important fundamental question of a mechanism of cooperative (concerted) multielectron transfer versus stepwise electron transfer has to be addressed. The paper offers a contribution along this line.

The photo-induced phase transitions are the phenomena, in which cooperativity is due to electron-phonon coupling. An excited electron relaxes causing a local lattice distortion and by the gain of deformation energy it is energetically easier to excite a neighboring electron. Photogenerated electronic excitation proliferates during the lattice relaxation. This is an essence of «domino effect» caused by the electron-phonon coupling, and nicely illustrates the cooperativity in one-dimensional systems [7]. It is of our opinion that the importance of studies of the photo-induced phase transitions goes far beyond scientific curiosity within physics and extends into fields such as chemistry, biology, materials science, where model systems are required. It is an additional motivation for the studies.

2. Multielectron-Transfer in Mixed-Stack Compounds.

As an extreme case of the photo-induced phase transitions, already exotic phenomena, there is photo-induced multielectron transfer in mixed-stack organic compounds. It has been known for some time, that in some compounds, an intermolecular electron transfer can be induced by temperature, pressure [8] and light [9]. However, it is the recent years extensive research [10-14] that helped us to understand the phenomena as cooperative multielectron transfer, a model for electron transfer self-organization.

The quasi-one-dimensional architecture of the mixed-stack charge-transfer (CT) compounds with alternating electron-donor (D) and electron-acceptor (A) molecules, stimulates intermolecular electron transfer, which can be generated by light (usually