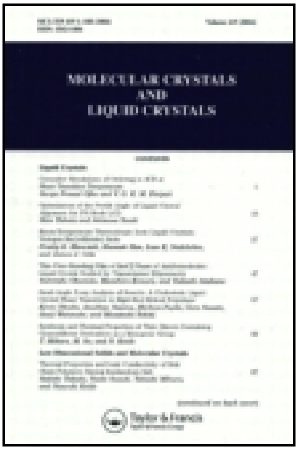

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PHENOMENOLOGICAL THEORY OF ELECTRON AND METHYL TRANSFER REACTIONS IN ORGANIC CRYSTALS

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Abstract A model description of intermolecular electron transfer and intramolecular electron transfer (and related to it methyl transfer) reactions in organic solids are discussed. As a first step towards quantitative modeling of the reactions we construct potential energy surface in the phonon normal coordinates space. A role of coupling of the transferred electron to intramolecular vibrations and excitons which determine dielectric properties of the crystal is stressed. Transformations "neutral-ionic" in TTF-Chloranil and zwitterion formation in Methyl p-Dimethylaminobenzenesulfonate are discussed as examples.

INTRODUCTION

The process of electron transfer in solution has long been studied and is well understood at present. The theory of the process is based on models of spin-boson type.[1] When an analogous process is considered in an organic crystal, one realize both, similarities and differences. If one wants to see more similarities than stresses "local" viewpoint and tends to consider an organic crystal environment as a solvent for a local transformation. On the other hand when differences are emphasized, one stresses "collective" nature of a solid state. In a sense, the views are reflected in two known phenomenological approaches used to understand qualitatively solid state reactions, topochemical postulate and phonon assistance. The approaches are without a theoretical background, thus are rather difficult to verify.[2] A need for a theoretical foundation for the reactions in organic solids is quite obvious. We shall advocate a local viewpoint and focus on a construction of a local potential energy surface for a cluster of molecules, surrounded by crystal environment. The potential energy surface determines activation energy and free energy difference , ΔF, for the local transformation. Than, the interface moves across the transforming crystal under the action of "chemical pressure" , $-\Delta F/\Delta V$, also expressed in terms of local strains.[3]

POTENTIAL ENERGY SURFACE

The essence of a chemical transformation is that reactants and products are different in electronic structures and nuclear configurations. The configurational space is defined by intramolecular (Q) and intermolecular (q) normal coordinates. For the electron transfer process, characterized by a dipole moment, μ, dielectric properties of a crystal are important and they will be described by electric field variable, $\varepsilon(p)$, expressed by normal coordinates of excitons (p).

Let us consider a centrosymmetric array of alternating electron donors (D) and acceptors (A). We are interested in the reaction:

$$\ldots A\ D\ (\underline{A}^{-}\underline{D}^{+})_n\ A\ D\ldots$$

$$\ldots A\ D\ A\ D\ A\ D\ A\ldots$$

$$\ldots A\ (\underline{D}^{+}\underline{A}^{-})_n\ D\ A\ D\ldots$$

reactants products

The states corresponding to electronic structure of reactants and products are denoted as $\langle N|$ and $\langle I_n +|$, $\langle I_n -|$, respectively. The ionic products are characterized by opposite polarization and structural changes, often called dimerization (a break of center of inversion symmetry). The n-fold electron transfer between adjacent molecules cost energy (per a DA pair),

$$\delta_n = \delta - \alpha(n)J \tag{1}$$

where $\delta = (I-A)$ is the difference between ionization potential (I) of D and electron affinity (A) of A molecules, $\alpha(n)$ is the n-dependent Madelung constant for a linear chain[4] and J is the Coulomb integral for the pair of ionized molecules. The potential difference, δ, depends linearly on totally symmetric <u>intramolecular</u> deformations[5], thus, $\delta=\delta_0 + gQ$, where g is a coupling constant and Q is the normal coordinate of totally symmetric (A_g) intramolecular vibration. The Coulomb interaction, J, on the other hand depends on antisymmetric <u>intermolecular</u> deformations (structural changes)[5], with a pattern of an antisymmetric (A_u) lattice mode, given by normal coordinate q.

Finally, the dipole (μ) created by the transferred electron interacts with an electric field,

$$\varepsilon = \Sigma c_j p_j\,, \tag{2}$$

expressed as a linear combination of electronic excitons normal coordinates, p_j.

Taking into account all the above mentioned couplings, the n-fold transfer of an electron in the ...DA... chain costs energy,

$$H_e = \delta^0{}_n + gQ + \sigma(\beta q + \mu\varepsilon). \tag{3}$$

$\delta^0{}_n$ denotes energy of n-fold charge transfer excitation in the absence of any coupling, and $\sigma = (+,-)$ denotes polarization of the ionic state. The crystal, more precisely, a surrounding of a cave where the electron transfer process occurs, will be characterized by harmonic oscillators,

$$H_b = 1/2\,\Omega^2Q^2 + 1/2\,\omega^2q^2 - kq\varepsilon + 1/2\,\chi^{-1}\varepsilon^2\,. \tag{4}$$

χ has a sense of electronic (high frequency) susceptibility and k couples intermolecular vibrations to the electric field (the effect being represented in "shell models" of lattice dynamics). It is important to notice that higher order couplings, like Qq^2, may be introduced and they lead to molecular compressibility concept.[5] The "fast" variables, ε and Q, can be eliminated from the total hamiltonian, $H_b + H_e$, with the result,

$$H = 1/2(\omega^2 - k^2\chi)q^2 + \delta(n) + \sigma(\beta + \mu k\chi)q\,, \tag{5}$$

where,

$$\delta(n) = \delta^0{}_n - 1/2\,\mu^2\chi - 1/2\,g^2\Omega^{-2}. \tag{6}$$

The second term in (6) is clearly responsible for "solvation" energy and can be called a polarization correction to the electronic excitation energy, $\delta^0{}_n$. The last term in (6) is the molecular deformation energy. Both energies are stabilizing for the electron transfer process. The frequency of the lattice mode responsible for intermolecular deformation is now renormalized in the same way as in the dielectric theory of molecular crystals,[6] leading to $(\omega')^2 = (\omega^2 - k^2\chi)$, eq.(5). Due to the coupling between intermolecular vibrations and the electric field, the electron transfer process now depends on the lattice deformation via coupling constant, $\gamma(\mu) = \beta + \mu k\chi$. It is important to notice the dependence of the coupling constant on the dipole moment of the ionic state. This gives new mechanism for the electron-phonon coupling in the charge transfer transformations in organic solids.

If one would be interested in photoinduced reaction leading to the products as indicated above, than the hamiltonian which is sufficient to describe the system and the process, is

$$H = |I_n\sigma\rangle\,(\delta(n) + \sigma\gamma(\mu)q)\,\langle I_n\sigma| + 1/2\,(\omega')^2q^2. \qquad (7)$$

The reactants state, $\langle N|$, is assumed as the ground state and the products states as the excited (double degenerate) state. One can then work with the hamiltonian (7) in the same way as shown by Nagaosa.[7] This approach would be of a great importance to understand very elegant experiments on photoinduced valence instabilities in TTF-Choranil crystals.[8]

However, when the electron transfer reaction is stimulated by temperature or pressure, one must assume some electronic interaction between redox orbitals of the reactants, e.g., $\langle N|I_n\sigma\rangle = -t(n)$, different from zero. The reaction path is then determined by ground state energy curve, $W_g(q)$,

$$W_g(q) = -1/2\,(\omega')^2q^2 + E_g(q), \qquad (8)$$

where $E_g(q)$ is a lowest eigenvalue of the electronic part of the hamiltonian, (5) written in the base of reactants and products states,

$$\begin{array}{cccc} & \langle N| & \langle I_n+| & \langle I_n-| \\ \hline & 0 & -t(n) & -t(n) \\ H_e(q) = & -t(n) & \delta(n)+\gamma q & 0 \\ & -t(n) & 0 & \delta(n)-\gamma q \end{array} \qquad (9)$$

The analytical expression for the lowest eigenvalue is,[9]

$$E_g(q) = 1/3\,[\delta(n) + 2G^{1/2}\cos(\phi + 2/3\pi)] \qquad (10)$$

where $G = \delta^2{}_n + 3(\gamma q)^2 + 6t^2$, $\phi = 1/3 \text{ arc} \cos(KG^{-3/2})$, $K = \delta(n)[\delta^2(n) - 9(\gamma q)^2 + 9t^2]$. The ground state energy, $W_g(q)$, may show one, two or three minima, depending on the important parameters, $\delta(n)$, γ and ω', assuming $t(n)$ is non zero. The minima of the ground state energy indicate stable (metastable) configurations of the crystal lattice, and values of the coordinate $\langle q\rangle$ which correspond to the minima, measure the structural changes. At this point one should notice similarity of the problem discussed here to that elaborated by Toyozawa[10] and represented by the famous T-U-S triangle (in analogy to "alchemical triangle" introduced by Chakraverty[11]). For a representation of our results, the triangle $\delta(n)$ - ω' - γ should be used. The important observation is that, as it was shown by Toyozawa , one passes from single minimum via three minima to two minima energy curves, when increasing coupling constant, γ.

In the limit $t(n) = 0$, the activation energy for the considered electron transfer, is easily estimated as,

$$\Delta E_{act} = [\delta(n)]^2 (4\Delta E_{def})^{-1} , \qquad (11)$$

where ΔE_{def} stands for the energy of lattice deformation, which is $1/2\gamma^2(\omega')^{-2}$. Condition for stability of the product is, $\delta(n) < \Delta E_{def}$. It is important to notice that the "least motion" principle, when expressed within the presented theory, means that mechanically stiff crystal lattice is more susceptible for a reaction than a soft one. The stiff lattice assure smaller lattice deformation, $<q>$, larger deformation energy, therefore smaller activation energy. This conclusion is somewhat intriguing and opposite to the one commonly accepted in relation to phase transition phenomena. The studies by Stezowski and Eckhardt on the solid state reaction in 2,5-distyrylpyrazine,[2] may be seen as a first experimental indication that the conclusion is correct. In the concerted X-ray crystallographic and polarized Raman studies, they have found that the highest B_{2g} lattice mode is related to structural changes induced by the reaction.

EXAMPLES

The TTF-Chloranil, a charge transfer crystal, is known to show the temperature, pressure and photoinduced transformation, which can be treated as the reaction, represented by the above scheme. The transformation is called "neutral-ionic" phase transition [5]. For the system, we adopt the following values of the parameters. The Franck-Condon excitation energy for a cluster of n transferred electrons in a chain is, $\delta(n)=4.08 -2.77\alpha(n)$ eV (according to ref.[12]). The overlap integral for the cluster can be approximated by $t(n) = t^n{}_0$,(according to ref.[4]) where t_0 is the overlap integral for a pair of DA molecules and is commonly assumed to be about .2 eV for the TTF-Chloranil pair. The lattice frequency, ω', is taken from the lattice dynamics calculations[13] and for the A_u ,B_u modes the frequencies are in the range 35 - 120 cm^{-1}. It corresponds to force constants values between .5 and 5 eV/A^2 . There is a real difficulty to estimate the coupling constant β or the effective one, γ. We assume γ to be in the range 1.5 - 3.0 eV/A. Taking ω' equal 100 cm^{-1} (force constant equal 4 eV/A^2) we show on Figure 1, the ground state energies calculated for different coupling constant, γ, and number of molecules, n, in the cluster which undergoes the transformation. The calculated ground state energies are representative for TTF=Chloranil system.

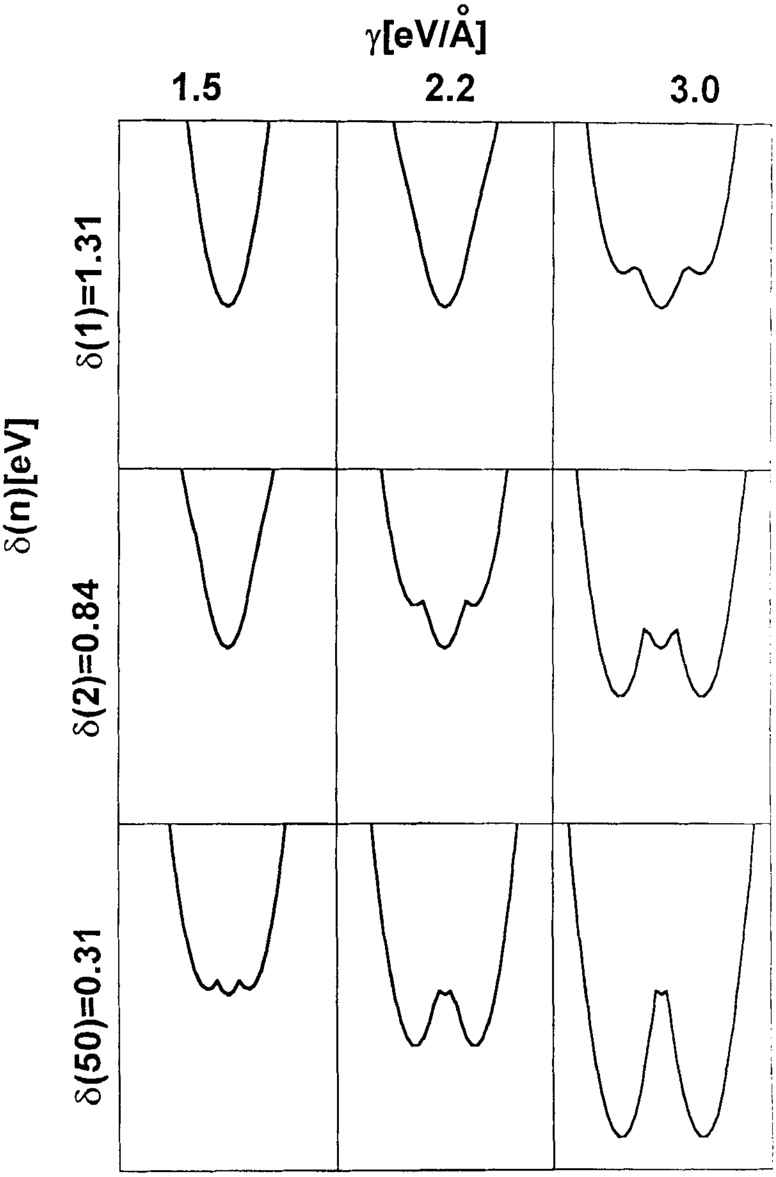


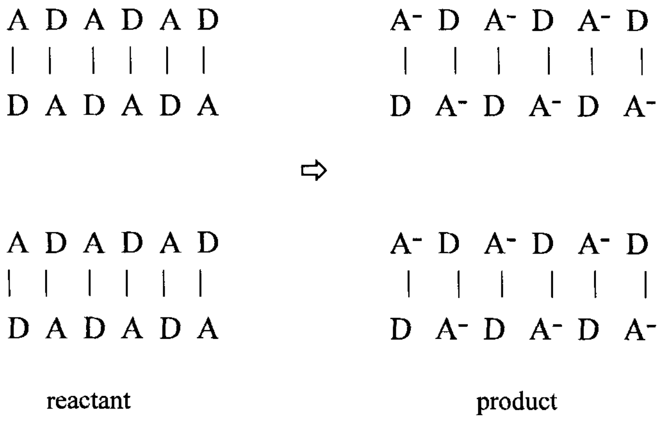
Figure 1. Local ground state energy for intermolecular electron transfer process as a function of lattice distorsion (q) calculated for several parameters (γ, δ(n)).

We may notice that the lattice deformation energy varies from .28 eV to 1.12 eV, for the assumed range of lattice frequencies. If δ(n) is taken to be .6 eV (approximately the energy of CT state near the neutral-ionic transition) than the energy barrier for the transition to ionic products is estimated to be .08 eV (930K) for the lower limit. Obviously, both quantities, the Franck-Condon energy, δ(n), and even more important, the coupling constant are critical for the quantitative estimation of the energetics of the transformation.

As an example of the intramolecular electron transfer, we take the temperature induced transformation in the crystal of Methyl-p-Dimethylaminobenzenesulfonate.[14] The transformation,

$$(CH_3)_2N\text{-}\phi\text{-}SO_3CH_3 \quad \Rightarrow \quad (CH_3)_3N^+ - \phi\text{-}SO_3^-$$

in the crystal can be represented by the following scheme,



The crystal structure of the reactant ($P2_1/c, z=4$) contains stacks (horizontal on the above scheme) of molecules nearly ideally oriented for the methyl transfer between A group ($-SO_3CH_3$) and D group ($-N(CH_3)_2$) of the nearest molecules in the stack. The intermolecular methyl transfer is accompanied (driven ?) by the intramolecular electron transfer, as indicated on the scheme. The product structure ($Pnc2, z=8$) contains chains (vertical) of molecules, strongly coupled (head to tail) by the ionic interactions. Each chain is surrounded by others with opposite polarizations.

The energy surfaces can be described, essentially by the same hamiltonian as above, with a modification that due to the methyl transfer between chains with opposite polarity, we introduce the overlap integral $\langle I+ | I- \rangle = T$. Despite of the fact, that it is one of best known examples of solid state organic reaction, we have less information about the parameters which enters the theory. In particular we do not know values for the electronic on-site energy for the electron transfer, δ. On the other hand it has been suggested[15] that the lattice mode of frequency around 30 cm^{-1} plays an important role in the transformation.

CONCLUSIONS

We have intended to show that the electron transfer reactions in organic solids can be understood within the theory which is based on couplings of the transferred electron to lattice phonons (as the primary effect) and to intramolecular vibrations as well as to excitons (as the secondary effect). In fact both effects are coupled together and this gives new mechanism for the electron-phonon coupling and increases strength of the coupling. The theory predicts that:

- the activated transformations will take place for sufficiently strong coupling between transferred electron and lattice modes which are responsible for structural changes.
- mechanically stiff lattice is preferred for the "least motion" principle[16] (known also as topochemical postulate[17]) and low activation energy for the reaction.

Numerical calculations with parameters representative for the TTF-Chloranil crystal indicate that the theory gives physically reasonable values for the quantities like activation energy and lattice deformation. It is also shown that the same theory can be used to understand, in the model categories, the zwitterion formation reaction in the Methyl-p- Dimethylaminobenzenesulfone. The considerations presented should be seen as a step towards quantitative theory of organic solid state reactions.

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