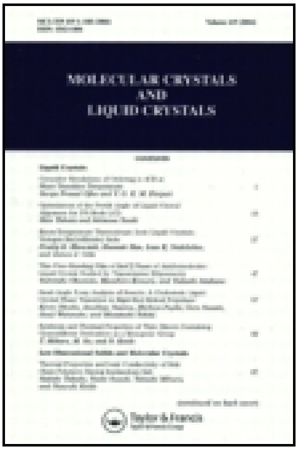

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ELECTRON INDUCED TRANSFORMATIONS IN ORGANIC MIXED-STACK COMPOUNDS AS MODELS FOR SOLID STATE CHEMICAL REACTIONS

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Abstract Recently discovered and extensively studied transformations, quasi-neutral mixed-stack of donor and acceptor molecules ↔ quasi-ionic dimerized stack in charge-transfer crystals has been treated as a solid state chemical reactions.

INTRODUCTION

The architecture of the organic charge-transfer (CT) crystals, two-component materials, is determined not only by the close packing principle but also by molecular energetics-the difference between ionization potential of a donor (D) and electron affinity of an acceptor (A) molecule. The difference, (I-A), can be identified as a hardness of the DA pair for an electron density transfer and is a measure of chemical reactivity. Here, it is the formation of the ionic dimer,

$$(D + A) = (D^+A^-) \qquad (1)$$

For large hardness, e.g., when it is greater than effective Coulomb interaction, J, between the pair of molecules, $(I-A) > J$, equilibrium in the process (1) will be shifted to the left and the ground state will be predominantly neutral and vice versa. The condition, I-A = 2J, is known as a "neutral-to-ionic" boundary.[1] Due to a non-zero overlap integral between HOMO of D and LUMO of A molecules, every state of equilibrium for the reaction (1) is a mixture of neutral and ionic configurations and the degree, ϱ , of the ionic admixture is generally identified as an average degree of CT (ionicity) for the organic materials.

In the mixed-stack crystals with predominantly neutral ground states the D and A organic molecules are arranged alternately along a stacking axis. It has been discovered recently[2-11], that the transformation, regular ↔ dimerized stack, in the compound tetrathiafulvalene-chloranil (TTF-CA) is accompanied by a change in degree of ionicity. The transformation, called "neutral-to-ionic", can be pressure[6-8,10] and temperature[2-5,9,11] induced and is a unique electron-induced structural transition. Theoretically, the transformation has been treated by models which were based on collective mechanisms (electron-phonon coupling),[12-15] and were unable to explain consistently all experimental facts. A need for a completely different approach has been advocated.[16]

Here, we would like to exploit conceptual similarities between the electron induced transitions and chemical reactions in the organic solid state. To do this we shall treat the "neutral-to-ionic" transformation as a solid state reaction.

THE MODEL

We treat the transformation as a non-collective process in two steps. The first, an initiation,

$$\ldots D\ A\ D\ A\ D\ A \ldots \quad \text{--} \quad \ldots D\ A\ \underline{D^{+}A^{-}}\,D\ A \ldots \qquad (2)$$

is a creation of an ionic dimer. The state on the right hand side of (2) is a frozen polar-exciton.[17] The second step for the reaction, a growing process of the dimerized ionic phase at the expense of the parent non-dimerized phase can be seen as a motion of neutral-ionic domain walls,

$$\ldots D\ A\ D\ A \big| \underline{D^{+}A^{-}}\,\underline{D^{+}A^{-}}\,\underline{D^{+}A^{-}} \big| D\ A\ D\ A \ldots ,$$

a concept already introduced in the theory of the transformation.[12]

The first step - a local dimerization

The essential condition for occurance of intermolecular solid-state topo-chemical reactions requires a minimum change in the form of the "reaction cavity". Thus a local dimerization has to be of a displacive type. This means an instability of a DA pair with respect to the stretching (intra-CT) mode. It has been shown[16] that the instability can be due to a competition between direct intermolecular interactions and indirect ones, for which transfered and intermolecular bond electrons are mediators. The diagonal coupling between the electrons and the mode has been considered[16] and we shall make here a generalization for non-diagonal couplings. Following ref. 16, the Hamiltonian for a dimer is written as,

$$H_{Dimer} = H_{o} + H_{Coupling}\ , \qquad (3)$$

where

$$H_o = E\cdot\delta\hat{n} + \tau\cdot\delta\hat{B} + \frac{1}{2}\Big(\sum_{A,D}\omega^2_{A,D}Q^2_{A,D} + \omega_d^2 q^2\Big) \quad (4)$$

and represents the Hamiltonian for uncoupled electrons and vibrations. E is half of an energy of CT excitation, τ is an effective overlap integral. The electronic operators, $\delta\hat{n}$ and $\delta\hat{B}$, describe changes in degree of charge transfer, ς, and bond charge, respectively. The last two terms represent the elastic energy of the dimer, relevant for the problem e.g., the third term stands for the energy of totally symmetric intramolecular vibrations and the last term is the energy of the stretching intra-CT mode. The coupling Hamiltonian,

$$H_{\mathrm{Coupling}} = \beta\cdot q\delta\hat{B} + \Big\{\sum_D g_D Q_D - \sum_A g_A Q_A - \gamma\cdot q\Big\}\delta\hat{n}, \quad (5)$$

comes from linear dependency of the energy of CT excitons(E) on the normal coordinates of the vibrations (the last term) and of the transfer integral (τ) (the first term), where $g_{A,D}$, β and γ are coupling constants. Eq. (5) indicates that the intramolecular vibrations, as well as the intra-dimer mode, act as a perturbation for the electronic subsystem and induce changes in the degree of ionicity and bond charge. Within the linear response theory, assuming an adiabatic response of the electronic subsystem (static case), the changes are,

$$\begin{bmatrix}\langle\delta\hat{n}\rangle\\ \langle\delta\hat{B}\rangle\end{bmatrix} = -\begin{bmatrix}\chi_{CT} & (\chi_{CT}\chi_b)^{\frac{1}{2}}\\ (\chi_{CT}\chi_b)^{\frac{1}{2}} & \chi_b\end{bmatrix}\begin{bmatrix}\sum g_{A,D}Q_{A,D} + \gamma\cdot q\\ \beta\cdot q\end{bmatrix} \quad (6)$$

χ_{CT} and χ_b (charge-transfer and bond-charge, respectively), are static electronic susceptibilities of the DA pair, unperturbed by the vibrations.[16] On substituting eq.(6) into (5), the effective frequency, Ω_d, for the intra-dimer mode can be calculated from the total Hamiltonian (3). The result

$$\Omega_d^2 = \omega_d^2 - \left(\gamma\chi_{CT}^{\frac{1}{2}} + \beta\chi_b^{\frac{1}{2}}\right)^2 \left[1 - \chi_{CT} \cdot \sum_{A,D} \frac{g_{A,D}^2}{\omega_{A,D}^2}\right]^{-1} \qquad (7)$$

indicates that the frequency is renormalized due to the indirect interactions mediated by the charge transfered from D to A molecule and the bond charge. When the site symmetry of the dimer allows for a coupling of the totally symmetric intramolecular vibrations to the CT excitation, the indirect interactions are further renormalized by the term in square brackets of eq. (7). In such a case the stability limit ($\Omega_d \rightarrow 0$) can be reached easier and this can happen for a DA pair at imperfections of a crystal.

An immediate consequence of the local dimer formation ($\langle q \rangle \neq 0$) is an increase in both degree of ionicity and the bond charge, according to eq.(6). The dimer with increased degree of ionicity, bond charge and shortened intermolecular distance can be interpreted as a condensed polar-exciton.[17] Thus, the initiation of the chemical reaction is a process

$$\underset{(\varrho \simeq 0)}{\ldots D^{+\varrho}A^{-\varrho}D^{+\varrho}A^{-\varrho}D^{+\varrho}A^{-\varrho}\ldots} \longrightarrow \underset{(P = \varrho + \langle\delta\hat{n}\rangle \simeq 1)}{\ldots D^{+\varrho}A^{-\varrho}\underline{D^{+P}A}^{-P}D^{+\varrho}A^{-\varrho}} \qquad (8)$$

which locally (in the "reaction cavity") decreases energy of the mixed-stack. As follows from the microscopic mechanism, the dimer - a giant molecule ($D^{+P}A^{-P}$) which forms a new phase will be characterzed by a predominantly covalent bond if $\beta \gg \gamma$ or the dimer will be predominantly ionic if $\beta \ll \gamma$. A mixture of both kinds of bonds forms a dative structure of the dimer.

The second step - a growth of the dimerized phase

A growth of the new phase, dimerized and ionic, has to be a highly non-collective process and the easiest way to visualize it would be motion of neutral-ionic, undimerized-dimerized domain walls. The crystals which are sensitive to the discussed neutral-ionic transformation will be seen as homogeneous or inhomogeneous of ionic and neutral molecules (in TTF-CA, the ionic phase being dimerized) and the degree of ionicity for the crystal means the time and space average ionicity of the mixed-valence D and A molecules. Thus, the average degree of ionicity, ϱ, has to be understood as a mean-field parameter of the system. The ground state of such a crystal is therefore a state of dynamical equilibrium for the process,

$$\ldots D\ A\ D\ A\ D\ A\ \ldots \begin{array}{l} \nearrow \ldots\underline{D^{+}A^{-}}\,\underline{D^{+}A^{-}}\,\underline{D^{+}A^{-}}\ldots \\ \searrow \ldots\underline{D^{+}}\,\underline{A^{-}D^{+}}\,\underline{A^{-}D^{+}}\,\underline{A^{-}}\ldots \end{array} \tag{9}$$

The dynamics of the neutral-ionic domain walls (interfaces) will be essential for an average structure of the system seen by diffraction methods. Moreover, the equilibrium (9) can be shifted by pressure or temperature. The energy barrier, $\Delta H^{\ominus}$, between neutral and ionic phases will determine the dynamics of the domain walls. At high temperatures, the thermal fluctuations allow overcoming the barrier and the walls move fast. When the temperature decreases, the energy barrier becomes smaller but there are smaller thermal fluctuations and the domain walls are move slower. The neutral-ionic "disorder" becomes more and more static, however, still not as static as to be clearly detected by diffraction methods.

It is important to realize that the change in the concentration of the ionic phase with temperature (increase with decreasing temperature) can be explained by Le Chatelier's principle applied to the equilibrium (9) with $\Delta H^{\ominus} < 0$. However, this simple rule cannot explain a discontinuous change in ionicity observed in TTF-CA crystals at about 80 K. Even, if one would assume the energy difference $\Delta H^{\ominus}$ to be dependent on the degree of ionicity (collective interaction between ionic domains), for a linear function, $\Delta H^{\ominus} = a + b\varrho$, the Le Chatelier's principle,

$$\left[\frac{\partial \ln\left(\frac{\varrho}{1-\varrho}\right)}{\partial T}\right]_p = \frac{\Delta H^{\ominus}(\varrho)}{kT^2} \qquad (10)$$

gives results identical to those obtained by Merrifield[18]. The result was that for system represented by molecules D^+ and A^- and treated as a set of $N\varrho$ holes distributed among N donors, and $N\varrho$ electrons among N acceptors, a transition can occur from a stack of smaller ionicity below the transition temperature to one of larger ionicity above. The temperature induced transformation in TTF-CA crystals is just the opposite.

Le Chatelier's principle is helpful when one discusses the influence of pressure on the equilibrium (9) for TTF-CA. The change in volume, $\Delta V^{\ominus}$, of the pure phases (per complex molecule) is negative due to dimerization. An increase of pressure shifts the equilibrium (9) to the right and the degree of ionicity increases, as experimentally observed.[6,7] The monotonic increase of the degree of ionicity up to 11 kbars can be reproduced very accurately by the function,

$$\varrho = \left\{1 + A \exp\left(- \frac{\Delta V^{\ominus}}{kT}\right)\right\}^{-1} \qquad (11)$$

with constants $A = 2.57$ and $\Delta V^{\ominus} = -5$ Å^3, fitted to the points ϱ (p=0) and ϱ (p=11 kbars). The volume difference is approximately 1% of the volume of TTF-CA pair, the contraction estimated from X-ray measurements, due to dimerization.[2] This simple analysis indicates that TTF-CA crystal behaves with pressure as a binary system (neutral and ionic domains) where the dynamical equilibrium is shifted by the pressure.

CONCLUSIONS

In spite of the fact that the recently discovered transition: (mixed, quasi-neutral stack) ⟷ (dimerized, quasi-ionic stack) in the TTF-CA system is of an unusual kind and cannot be interpreted by any simple theory of phase transitions, we have made an attempt to treat the transformation as a chemical reaction. A microscopic mechanism for the initiation step as a local dimerization has been elaborated. The TTF-CA crystal is treated as a binary system, where concentration of ionic dimers determines an average degree of ionicity. Under external conditions (p,T) there is a dynamical equilibrium between substrates (D^o and A^o molecules) and products (D^+A^- dimers) due to motion of domain walls between the two phases. A change in the degree of ionicity with increasing pressure can be understood with the simple Le Chatelier′s principle and the discontinuous change at 11 kbars could be interpreted as due to collective behaviour of the system above some critical concentration. The behaviour of the system with temperature can be interpreted in terms of Le Chateler's principle up to the discontinuity in ionicity, assuming the energy change for the reaction "neutral-ionic" is negative. The abrupt change in ionicity at 80 K observed in the TFF-CA crystal cannot be explained in terms of a simple, linear dependency of $H^{*}(\varrho)$. It is concluded that a very special collective interaction is switched on in the system at the temperature induced transition.

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