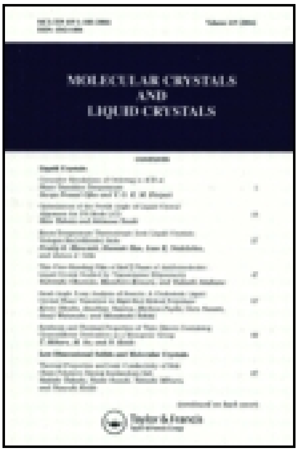

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ELECTRON INDUCED TRANSITIONS IN MOLECULAR SOLIDS

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Abstract The transitions in molecular solids, which are induced by electronic degrees of freedom (charge fluctuations, excited molecules), are considered from a point of view of a competition between direct and indirect energy contributions. The indirect interactions, which follow from electron-vibration (phonon) coupling, have two effects, static and dynamic. The static effect is due to phonon-mediated indirect interactions while the dynamic one results from the electron-mediated interactions. The effects are discussed, first for a dimer of molecules, to clarify microscopic mechanisms of the interactions, than generalization for many-body system is made. The neutral-ionic transitions, stability of solids "under chemical pressure" and photo-induced transitions are discussed.

INTRODUCTION

The electron-induced transitions in molecular solids are direct consequences of incipient electronic and/or structural instabilities. They are usually discussed in terms of a competition between electron transfer, electron-electron and electron-phonon interactions.[1] In particular, the electron-phonon coupling leads to instabilize ground states into completely different states, often accompanied by symmetry breaking (the Peierls transition, for example).

In molecular solids the transitions can be viewed as three-step processes. The first is self-trapping of an electronic excitation due to molecular deformation energy. The second step is local lattice deformation and the third is bulk structural change accompanied by electronic charge redistribution (charge density wave, CDW). The three steps represent an increasing order of catastrophe of an elementary electronic excitation in deformable lattice of deformable (!) molecules. Schematically, the cascade of the instabilities is represented in Fig. 1, taking as an example the charge-transfer (CT) exciton.

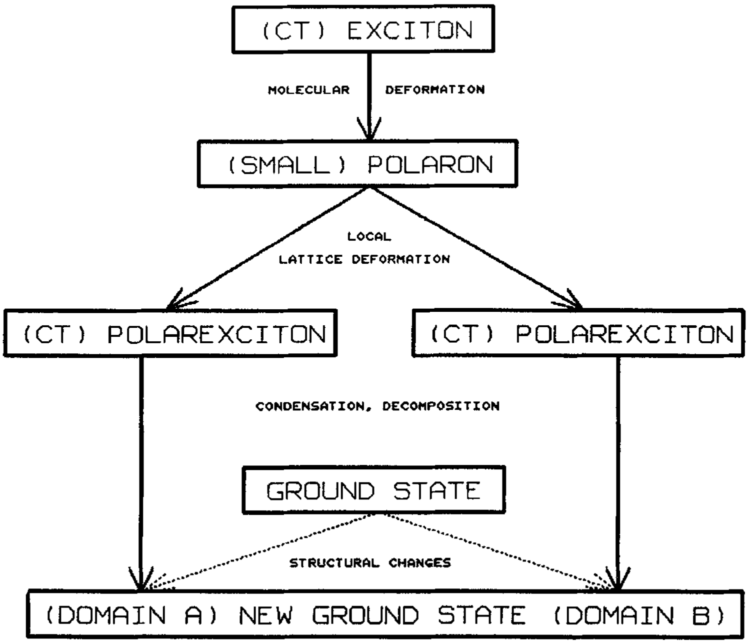

FIGURE 1 A cascade of instabilities of (CT) exciton in deformable lattice of deformable molecules.

The energies of deformation which tend to stabilize the new ground state are the indirect molecular interactions mediated by phonons. The photo-induced structural changes[2] are good examples of the phase transitions. On the other hand, the temperature or pressure induced structural changes, accompanied by electronic charge redistribution, are conveniently described as local or bulk mechanical softening of a crystal lattice due to electron-mediated interactions, where the electronic excitations are treated as virtual ones. The neutral-ionic transformations in mixed-stack CT crystals[3] seem to be good examples. There is variety of molecular systems, where the observed transitions can be interpreted within the suggested "classification" and used as examples, but it seems to me that the mixed-stack CT crystals, where both, photo-induced valence instability[4] and temperature (pressure)-induced neutral-ionic transition[5] have been observed (the TTf-Chloranil complex, for example), are the best model systems.

DIMER MODEL *(the first two steps)*.

We consider a chain of alternating donor (D) and acceptor (A) molecules - the mixed-stack. The D and A molecules have different on-site potentials and they symbolize not only chemically different molecules but also those which are crystallographically or structurally (defects) inequivalent. Usually, the lowest electronic excitation in the chain is the CT excitation, Fig. 2. Let us consider the DA dimer.[6]

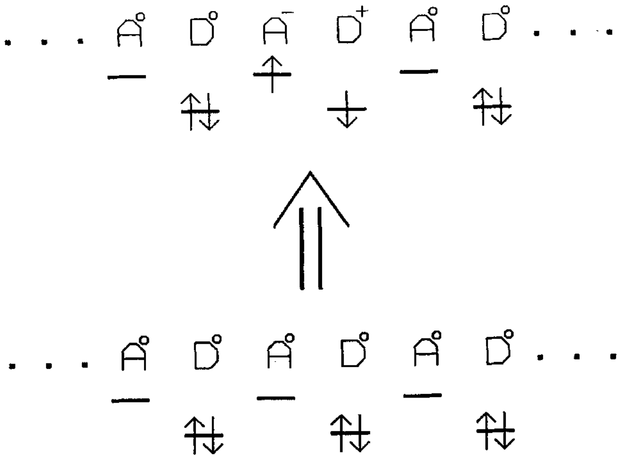

FIGURE 2 Charge-transfer excitation from neutral ground state of the DA chain.

The electronic states in the system are determined by three essential parameters,

- the on-site potential, $\alpha = (I - A)$, which measures the difference between ionization of D and electron affinity of A molecules,
- the inter-site Coulomb interaction, J, being the interaction between the electron distributed over A and the hole distributed over D, (the nearest to A in a chain),

- the interaction between ground and the CT state, measured by an overlapp integral, t.

The DA dimer is described by Hamiltonian, which contains two parts, electronic (CT) and vibrational (v),

$$H = H_{CT} + H_{v}, \tag{1}$$

where,

$$H_{CT} = (\alpha - J)\rho + t\cdot b \tag{2}$$

with the charge-transfer operator, $2\rho = 2 + n_A - n_D$, $n_i = \sum_\sigma a^+_{i,\sigma} a_{i,\sigma}$. The expectation value, $\langle\rho\rangle$, measures the molecular ionicity. The bond-charge operator, b, is $b = \sum_\sigma (a^+_{A,\sigma} a_{D,\sigma} + a_{A,\sigma} a^+_{D,\sigma})$. For the first excited, CT state, the Hamiltonian gives energy,

$$E_{CT} = (\alpha - J) + f(t), \tag{3}$$

where f(t) is a second-order correction, dependent on the overlapp integral.[7,8]

The essence of the electron-vibration coupling for the system is in modulation:

- the on-site potential,

$$\alpha = \alpha_o + \sum_A g_A Q_A + \sum_D g_D Q_D,$$

by a set (in the equations denoted as A and D) of totally symmetric intra-molecular vibrations with normal coordinates, $Q_{A,D}$.

- the Coulomb interaction, J, by the inter-molecular vibrations,

$$J = J_o + \sum_n \gamma_n q_n,$$

with normal coordinates, q_n.

- the overlapp integral by the inter-molecular vibrations,

$$t = t_o + \sum_n \gamma_n q_n.$$

The vibrational part of the Hamiltonian is,

$$H_v = \frac{1}{2}\Sigma_{A,D}(\dot{Q}^2_{A,D} + \omega_{A,D}Q^2_{A,D}) + \frac{1}{2}\Sigma(\dot{q}^2_n + \omega_n q^2_n). \qquad (4)$$

The main features of the dimer model are conveniently disscused assuming that the transfer integral, t, is small and its effect can be neglected. The assumption is usually well satisfied in typical molecular crystals and so called weak CT solids. With the assumption, the equations of motion are,

$$\ddot{Q}^2_{A,D} + \omega_{A,D}\cdot Q_{A,D} = g_{A,D}\cdot\rho \qquad (5A)$$

$$\ddot{q}^2_n + \omega_n q_n = \gamma_n\cdot\rho \qquad (5B)$$

Now, we shall consider static and dynamic consequences of the electron-vibration couplings.

Static Effect.

The static effect is due to the fact that the ground state average, <ρ>, the molecular ionicity, is non zero and therefore there are intra-molecular deformations,

$$\sum_{A,D}<Q_{A,D}> = -\sum_{A,D} g_{A,D}\cdot\omega^{-1}_{A,D}\cdot<\rho>, \qquad (6)$$

and the inter-molecular deformation,

$$\Sigma_n<q_n> = -\Sigma_n\gamma_n\cdot\omega_n^{-1}\cdot<\rho>. \qquad (7)$$

The static molecular defromations, being of opposite sign for D and A molecules (an expansion of the acceptor and a contraction of the donor), do increase the site non-equivalence measured by potential α. An important role of the molecular deformation, induced by the electron transfer has been demonstrated for so called segregated-stack systems.[9,10] In particular, it has been shown (and verified experimentally) that the molecular distortions stabilize predominantly the CDW in organic metals (TTF-TCNQ, for example). The molecular deformations, related to the degree of ionicity, although difficult to be measured precisely, have been noticed (TTF-Chloranil, for example[11]).

The important consequence of the discussed deformations is in a decrease of the electronic excitation energy, (here the CT state), the effect which is called self-trapping,

$$E_{CT} = E^0_{CT} - \sum_{A,D} g^2_{A,D}\cdot\omega^{-1}_{A,D} - \sum_{A,D} \gamma^2_n\cdot\omega^{-1}_n. \tag{8}$$

The second term,

$$\sum_{A,D} g^2_{A,D}\cdot\omega^{-1}_{A,D} = \sum_{A,D} \lambda_{A,D} = \lambda_{S(ite)}, \tag{9}$$

represents energy gained by the dimer due to the molecular, totally symmetric deformation. The enrgy is often called small-polaron binding energy. The third term,

$$\sum_n \gamma^2_n\cdot\omega^{-1}_n = \sum_n \lambda_n = \lambda_{B(ond)}, \tag{10}$$

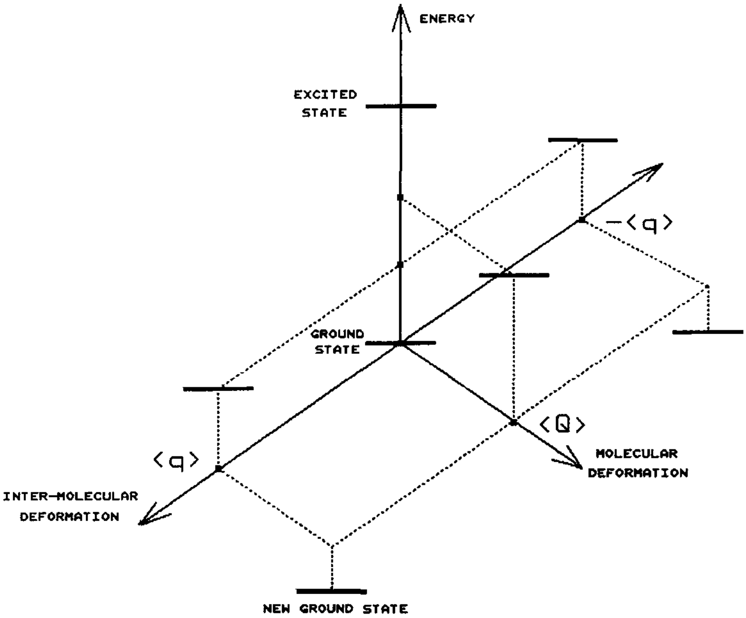

FIGURE 3 Schematic representation of molecularand intermolecular trapping of an excited state.

is the binding energy of the CT polaron. Both energies of deformation,

λ_S and λ_B, are indirect interactions mediated by the vibrations of the considered dimer. When the energies overcome the excitation energy, the new ground state is formed (Fig. 3). The solid-state photodimerization of anthracene, which is favoured at crystal defects,[12] may serve as an example. More trivial, but important example could be CT excitation in KCl crystal. The transfer of an electron from Cl^- to K^+ ion result in lattice-relaxed (deformon) pair, Cl^0 and K^0. The existance of similar but more efficient mechanism qualifies silver halides as good photographic materials - exposure to light results in separation of Ag^0 atoms and halogens. Intermediary electronic and ionic processes are more complicated, but in any case the "oxidized" state (ionic state) is the ground state while the "reduction" is realized in the relaxed excited states (metastable). The neutral-ionic transition in mixed-stack CT crystals,[3,5] in particular photo-induced valence instabilities, recently observed in the systems,[4] are the molecular (organic) "analogue" of the transitions in the ionic crystals.

Dynamic Effect

The dynamic effects of the electron-vibration couplings are seen as changes in the dynamics of the system. The dynamics is described by fluctuations in the normal coordinates,

$$\delta Q_{A,D} = Q_{A,D} - \langle Q_{A,D}\rangle, \tag{11}$$

$$\delta q_n = q_n - \langle q_n\rangle. \tag{12}$$

The vibrations around static displacements drive fluctuations in the charge distribution, $\delta\rho$, and the relation will be assumed to be linear,

$$\delta\rho = -\chi_{CT}\cdot\Big(\sum_{A,D} g_{A,D}\cdot\delta Q_{A,D} + \sum_n \gamma_n\cdot\delta q_n\Big), \tag{13}$$

where χ_{CT} is the electronic (charge-transfer) susceptibility. The susceptibility is the key property and can be determined, in general, by electronic elementary excitation energies.

The normal modes, renormalized by the electron-vibration coupling, are the eigenvalues of the dynamical matrix,

$$\begin{pmatrix} F & g\,\chi_{CT}\,\gamma \\ \gamma\,\chi_{CT}\,g & D \end{pmatrix} \qquad (14)$$

with,

$$F_{A,D} = \omega_{A,D}\cdot\delta_{A,D} - g_{A,D}\cdot\chi_{CT}\cdot g_{A,D} \qquad (15)$$

and,

$$D_{n,m} = \omega_n\cdot\delta_{n,m} - \gamma_n\cdot\chi_{CT}\cdot\gamma_n . \qquad (16)$$

The terms dependent on the electronic susceptibility are the electron mediated interactions between the mechanical variables. The effect of the interaction is in decreasing energies of the normal modes, in two steps:

- via the direct coupling of the modes with electrons (the matrices F and D). It is interesting to notice that,

  $$\mathrm{Tr}(F) = \lambda_S^{-1} - \chi_{CT} \qquad (17)$$

  is the molecular compressibility.[13] The matrix F has been first introduced by Girlando[14] for the CT dimer model and than some generalizations have been made for so called periodic dimer.[15] Spectroscopic consequences of the coupling, seen predominantly in IR spectra of the mixed-stack CT crystals have been demonstrated (see ref.16, for example).
- via the indirect coupling of intra-molecular and inter-molecular modes (the off-diagonal matrices). This coupling depends, of course, on symmetry of the modes. It does exists for the isolated DA dimer[6] or for a crystal site where the symmetry has been broken due to defects.

Both contributions tend to instabilize the system against intramolecular or/and intermolecular motions. The molecular instability (the molecular deformation and related to it charge redistribution) happens when the molecular compressibility becomes infinite. The condition has been analyzed in the context of neutral-ionic transformation.[17] In general, however, the condition for an instability of the considered DA dimer is that lowest eigenvalue of the dynamical matrix (14) tends to zero.[6] This will cause local instability in a lattice. Now, the question is how the local transitions (instabilities) induced by fluctuations in the electron distribution, can be generalized for, or how they condense in, a crystal.

CRYSTAL *(the third step).*

Following the essential concept of a molecular crystal that it can be considered as a set of molecules, the crystal Hamiltonian is,

$$H = \sum_{l,k} H_k(Q_{lk}) - \frac{1}{2} \sum_{l,k} \sum_{l'k'}' g_{lk,l'k'} \cdot Q_{lk} \cdot Q_{l'k'} . \tag{18}$$

Q_{lk} is a variable assigned to molekule (lk), representing the molecule's motion and charge fluctuation. The Hamiltonian H_k determines intramolecular states of the molecules occupying site (k) in the crystal unit cell. The second term represetnts interactions (couplings) between the fluctuations, which are symmetry allowed. Within the mean field approximation, the generalized susceptibility of the crystal is, in the wave-vector (q), representation,

$$\chi(q,\omega) = [(\chi^0(\omega))^{-1} - g(q)]^{-1}, \tag{19}$$

where $\chi^0(\omega)$ is the single molecule susceptibility, determined by states of H_k.

Phonon Instabilities

Clearly, the crystal becomes unstable when a lowest eigenvalue of the inverse coupled susceptibility, $\chi^{-1}(q,\omega)$, becomes zero. The condition for the electronically driven instability can be written,

$$| \chi^{-1}_{\text{phonon}}(q,\omega) - g(q)\, \chi_{\text{electronic}}(q,0)\, g(-q) | = 0. \tag{20}$$

The result of the instability is collective structural change, according to a pattern of the phonon which became soft and related to it change in charge distribution according to the pattern of fluctuation which coupled with the phonon. This is a typical mechanism for any Peierls-like transition. When the charge fluctuations are of dipolar type, than,

$$\chi_{\text{electronic}}(q,0) = [\alpha^{-1}(0) - L(q)]^{-1}, \qquad (21)$$

is the dipolar dielectric susceptibility,[18] expressed via molecular polarizabilities and Lorentz tensor.[19] The instability driven by an incipient singularity in the dipolar electronic susceptibility has been considered as an analogue of Kohn anomaly in molecular crystals.[20] In case of CT crystals, the charge fluctuations which predominantly couple with phonons are of scalar type (the molecular ionicity !) and the electronic susceptibility for the crystal can be expressed via capacitances of the molecules.[21]

It is clearly seen that the electron mediated interactions are attractive in nature, they give induction (polarization) energy contribution to the Coulomb interactions in polarizable medium.[18] In some systems, the indirect, electron mediated interactions can overcome direct Coulomb interactions and lead to attraction of charge carriers. This mechansim for hole-hole attraction has been suggested[22] for the high T_c superconductors.

The phonon instabilities, driven by fluctuations in electronic system, result as structural phase transitions. The important sympthoms of the transitions are soft phonon modes. In fact, the concept of soft-mode, invented by W. Cochran in 1959, came out as result of so called "shell model" for ferroelectric crystals, where indirect, attractive contribution to interionic force constant has been described by the dielectric susceptibility as in eq. (21). However, there are very rare cases where almost complete softening of a phonon have been observed. There are many reasons for it, and a pinning of the soft phonon mode at structural defects being one of them. More often, one can observe soft-like behaviour of a phonon. This indicates discontinuous phase transition with mechanism as described above. Some examples of phase transitions, which are collective in nature with soft-like phonon sympthoms and driven by electronic degrees of freedom, can be found in CT complexes (K-TCNQ, TTF-MBDT).[23,24] The electronically driven soft-mode concept has been also exploited in case of the neutral-ionic transformation in TTF-Chloranil crystal,[25] but it has not been very promising.

"Chemical Pressure"

There are many processes, mechanisms of transformations, which cannot be explained within the collective picture (a softening of the bulk crystal) and require a local viewpoint. There are many concepts, which were invented to underline the role of local processes in solids, among them the local strain field produced by local perturbation (an instability). The perturbations are almost always of electronic (chemical) nature and the term "chemical pressure" is used to stress the main effect of the perturbation.[26] The chemical pressure can be produced by chemical reaction,[27] concentration of an impact energy (detonation) in energetic materials[28] or photo-induced local instabilities.[29] Some other electron-induced transformations (in the class of mixed-valence compounds[30] and local phase transitions in ferroelectrics with Jahn-Teller impurities[31]) are also treated from local viewpoint and an influence of a crystal environment on a molecule (a site) is considered as giant solvent effect.

Consider randomly distributed perturbations in a molecular crystal,[26] and assume the lattice gas model. Let $\{\sigma\}$ denote configuration of the perturbations and $x=\Sigma\sigma_l$, where $\sigma=0$ or 1, is the concentration. The concentration fluctuation, $x-\sigma_l$, at site (l) couples to the crystal lattice and generates displacement wave,

$$Q\Big(q,\{\sigma\}\Big) = -\chi_{\text{phonon}}\Big(q,\{\sigma\}\Big)\cdot g(q)\cdot\rho\Big(q,\{\sigma\}\Big), \tag{22}$$

where

$$\rho\Big(q,\{\sigma\}\Big) = N^{-1}\sum_l (x-\sigma_l)\exp(iqR_l),$$

is the Fourier transform of the concentration fluctuation, here considered as a variable. The coupling to the lattice is given by $g(q)$. In spite of the fact that the field, $g(q)\,\rho(q,\{\sigma\})$, and the generated static strain, $Q(q)$, are expressed in q-space, they are local, concentrated around the perturbations. It has to be noticed that the configurational average of the strains is zero. The strains, locally generated, give rise to lattice deformation energy,

$$\Delta V_{def}(\{\sigma\}) = \frac{1}{2} \Sigma\, \rho(q,\{\sigma\})\; g(q)\; \chi_{phonon}(q,\{\sigma\})\; g(-q)\; \rho(-q,\{\sigma\}) \qquad (23)$$

This is the indirect, phonon mediated, interaction between perturbations, measured by the concentration fluctuations. The energy tends to stabilize the particular configuration of the perturbations. If, $V_{ll'}$ denotes direct interaction between perturbations located at sites l and l', than stabilization of the particular configuration depends on the

$D^0 A^0 D^0 A^0 D^0 A^0 D^0 A^0 D^0 A^0 D^0 A^0 D^0 A^0 D^0 A^0$	Neutral State
$D^+A^-\; D^+A^-\; D^+A^-\; D^+A^-\; D^+A^-\; D^+A^-\; D^+A^-\; D^+A^-$	Ionic States (dimerized)
$D^+\; A^-D^+\; A^-D^+\; A^-D^+\; A^-D^+\; A^-D^+\; A^-D^+\; A^-D^+\; A^-$	
$D^+A^-\; D^+A^-\; D^+A^-\; D^+A^-\; D^+\; A^-D^+\; A^-D^+\; A^-D^+\; A^-$	Spin $\frac{1}{2}$ Soliton
$D^+\; A^-D^+\; A^-D^+\; A^-D^+\; A^-\; D^+A^-\; D^+A^-\; D^+A^-\; D^+A^-$	
$D^+A^-\; D^+A^-\; D^+A^-\; D^+A^-\; D^0\; A^-D^+\; A^-D^+\; A^-D^+\; A^-$	Spin - 0 (Charged) Solitons
$D^+\; A^-D^+\; A^-D^+\; A^-D^+\; A^0\; D^+A^-\; D^+A^-\; D^+A^-\; D^+A^-$	
$D^+A^-\; D^+A^-\; D^+A^-\; D^0 A^0 D^0 A^0 D^0 A^0\; D^+A^-\; D^+A^-$	Neutral - Ionic Domain Walls
$D^0 A^0 D^0 A^0 D^0\; A^-D^+\; A^-D^+\; A^-D^+\; A^0 D^0 A^0 D^0 A^0$	

FIGURE 4 Schematic representation of neutral and ionic states, solitons and domain walls in DA-chain (according to ref. 2)

total energy difference,

$$\Delta V(\{\sigma\}) = \frac{1}{2} \sum_{l,l'} \{x-\sigma_l\}\{x-\sigma_{l'}\} V_{ll'} - \Delta V_{def}(\{\sigma\}). \qquad (24)$$

This result indicates, that not only the concentration, x, can be a parameter for phase transition (system decomposition, for example), but also configuration of perturbations will be responsible for a transition (glass transitions, for example). An interesting illustration of instability against particular concentration fluctuation wave (configuration of perturbations) would be a CT crystal near the neutral-ionic boundary.[32] The distribution of ionized D^+A^- pairs in the crystal (along the mixed-stack) is the important aspect of the neutral-ionic phase transition. It is believed, following other arguments,[33] that it is energetically favourable to form clusters of the ionized molecules along the stacks (Fig. 4). The argument, however, is based only on the direct energy contribution,[34] without taking into account the deformation energy. More quantitative analysis of the pressure or temperature induced neutral-ionic phase transition has to include both effects.

Photo-induced Transitions

There is rapidly growing interest in a search for photo-induced structural phase transitions.[2,4,29] The general rule, that stability of a solid (instability) depends on a competition between direct energy contribution and indirect one, can be applied to study photo-induced structural changes.[26,29] The simplest approach is to assume that the direct energy contribution is only that required to introduce perturbations to the lattice, e.g. to excite molecules. Thus for a cluster of m neighbouring molecules, the change in crystal energy is,

$$\Delta V(m) = m \cdot E_{FC} - \Delta V_{def}(m), \tag{25}$$

where E_{FC} Franck-Condon excitation energy and the lattice deformation energy can be approximated by,

$$\Delta V_{def}(m) = m^2 \sum_q g(q)\, \chi_{phonon}(q,m)\, g(-q). \tag{26}$$

The essential feature of the competition between the energy contributions in eq. (25) is that the deformation energy, being many-body in character, is not additive like the direct one. The condition for energetic stability of the m-molecule cluster is,

$$E_{FC} < \left[\Delta V_{def}(m) - \Delta V_{def}(m-1) \right], \tag{27}$$

and the inverse inequality corresponds to metastability. Considerations along this line can be applied to transitions like photopolymerization, photoisomerisation, photochromism and photochemical hole burning.[35]

The energetic considerations do indicate a possible transition, but we need thermodynamics to describe observable transition. This can be conveniently done with the Ising model, assuming,

$$\sigma_l = +\frac{1}{2} \quad \text{for the excited state,}$$

$$\sigma_l = -\frac{1}{2} \quad \text{for the ground state.}$$

The effective Hamiltonian for the system is than,

$$H_{eff}(\{\sigma\}) = h \sum_l \sigma_l - \frac{1}{2} \sum_{l,l'} J_{ll'} \sigma_l \sigma_{l'}, \tag{28}$$

where the "field" is

$$h = E_{FC} - \frac{1}{2} \sum_q g(q)\, \chi_{phonon}(q)\, g(-q), \tag{29}$$

which is the energy of "deformon", "small polaron", "reaction cavity" or "hot spot", and

$$J_{ll'} = \sum_q g(q)\, \chi_{phonon}(q)\, g(-q) \exp iq(R_l - R_{l'}). \tag{30}$$

The model, as it is well known, can be solved by variety of methods. It is important to notice that for non-zero "field", there is possibility to observe "switching" phenomena and the phase transition takes place for h = 0. The "field" therefore should be interpreted as a temperature (pressure) dependent quantity, which changes sign at the transition point. Within the model, the photoisomerization (A-B transition) in polydiacetylenes has been discussed.[29]

Still simpler description of the electron induced transitions, due to a condensation of electronically excited molecules has been applied to dense magnetic (triplet) exciton systems (TCNQ ion radical salts[36]) and thermal charge-transfer transitions (TTF-TCNQ[37]). Free energy (per particle) of a system is written as,

$$f = a\,x + b\,x^2 + x \ln g - x \ln x - (1-x) \ln (1-x), \qquad (31)$$

with a being direct energy contribution, b - the indirect (phonon mediated) energy contribution (always negative), x - the average concentration of the excited molecules and g being degeneracy of the excited state. This description, however, would only be valid when the excitation energies are comparable with thermal energy.

CONCLUSIONS

The electron induced transitions are phenomena which uncover richness of the molecular (organic) materials. The transitions always follow from a competition between direct energy contributions and indirect ones. In molecular solids, this competition is on three levels: molecular, intermolecular (dimer) and structural, thus one can trace the three step cascade of electronically driven instabilities. The transitions have been classified as,

- temperature (pressure) induced instability of a phonon mode, due to electron mediated interactions,
- condensation of randomly distributed lattice-relaxed excitons or other perturbations ("chemical pressure"), due to phonon mediated interactions,
- photo-induced structural transitions following from a competition between excitation energy and lattice deformation (phonon mediated interactions).

The paper offers a unified description of the transitions and, it is believed that, contributes to deeper understanding of possibilities and impossibilities of various types of electron induced transitions in molecular solids. This will be useful in designing new materials with desired properties and functions, including molecules of various sizes. The laser induced phase transitions of non-thermal type seem to be most exciting for future studies, also for their almost unlimited possibilities of applications.

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