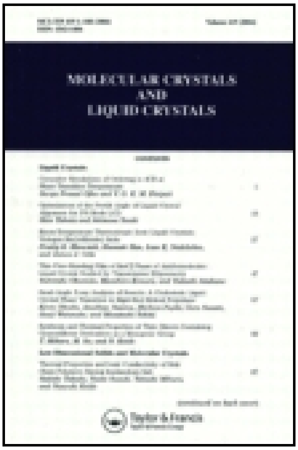

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Charge-Transfer Excitations In Partly-Inoic Complexes

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CHARGE-TRANSFER EXCITATIONS IN PARTLY-IONIC COMPLEXES

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Abstract The Mulliken dimer of admixed DA and D^+A^- configurations requires extensive generalization to solid complexes of π-donors (D) and π-acceptors (A) with many more configurations. Diagrammatic valence-bond techniques yield correlated crystal states that rationalize the cohesive energy of partly-ionic ($q \sim 0.50$) organic complexes, lead naturally to a q-dependent kinetic energy contribution, and produce charge-transfer (CT) excitations and intensities that differ significantly from dimer results for intermediate ionicity. CT spectra in solids are sensitive to interstrand Coulomb interactions that stabilize intermediate q relative to both neutral and ionic ground states.

INTRODUCTION

Molecular complexes of electron donors (D) and acceptors (A) occur in both solutions and the solid state. Mulliken associated[1] the strong new charge-transfer (CT) absorption of dimers with configuration interaction, or admixing, of neutral $|DA\rangle$ and ionic $|D^+A^-\rangle$ states. While other intermolecular interactions[2] also stabilize the dimer, the CT intensity goes as t^2, with

$$t = \langle D^+A^- | \mathcal{H} | DA\rangle \qquad (1)$$

Such configuration interaction (CI) becomes prohibitively more difficult in solid CT complexes containing N donors and N acceptors, even when the CT integral t is restricted to face-to-face stacks of planar π-donors D and π-acceptors A. Realistic descriptions of CT solids nevertheless require correlated crystal states[3,4] involving many configurations. The neutral-ionic transition of D = tetrathiafulvalene (TTF) and A = chloranil explored by Torrance et al[5] and others,[6] in particular, demands such admixtures of nearly degenerate neutral and ionic configurations.

Diagrammatic valence bond (VB) methods[7,8] yield exact, or fully correlated, states for quantum cell models with $N_e \approx 12$-14 electrons. The basic restriction to one Wannier orbital ϕ_p per site is readily adapted[9] to CT solids by choosing the highest occupied molecular orbital (HOMO) for D sites and the lowest unoccupied molecular orbital (LUMO) for A sites. Indeed, we may choose[10] the site functions in Fig. 1 to be exact ground states of isolated D, $D^+\sigma$, D^{+2} or A, $A^-\sigma$, A^{-2} species. These states are hardly perturbed on forming molecular solids, as shown by vibrational and optical studies, and readily incorporate electron transfers via t. We consider in this paper the stability and spectra solid complexes at intermediate ionicities, where both finite t and interchain Coulomb interactions are important.

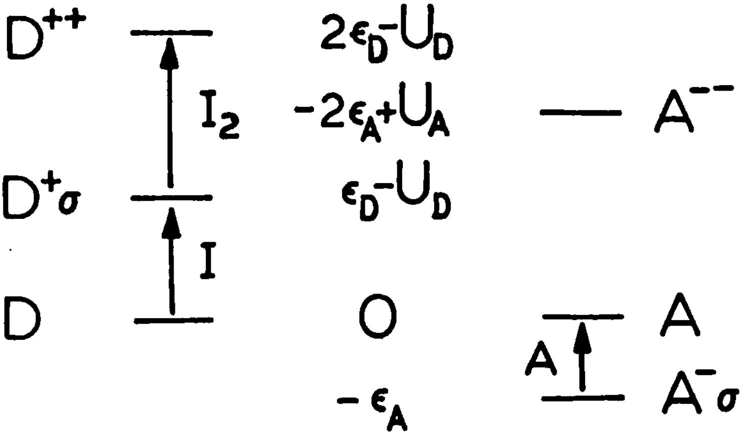

Fig. 1. Energies of donor and acceptor sites for empty, singly-occupied, and doubly occupied ϕ_p.

When $|DA\rangle$ and $|D^{+}A^{-}\rangle$ are degenerate, the dimer ground state $D^{+q}A^{-q}$ has ionicity q = 0.5 and a CT absorption at $2\sqrt{2}|t|$. Dimers and effective dimers still provide insights about the q-dependence of vibrational, optical, or magnetic properties, even in mixed regular stacks whose equally strong transfers to both neighbors sharply limit quantitative applications.

Models for CT solids have so far been primarily of conceptual interest. McConnell et al. introduced[11] a Hartree approximation for Coulomb interactions in partly-ionic solids, thereby entirely neglecting instantaneous charge correlations. Straightforward arguments then show that only neutral ($q \approx 0$) and ionic ($q \approx 1$) ground states are possible, as indeed observed in many weak complexes and a few strong complexes, respectively. But subsequent evidence for intermediate q in TTF-chloranil, in[12] dimethylphenazine-TCNQ, and in many segregated-stack conductors like TTF-TCNQ clearly require explicit consideration of correlations.[8] The $t \rightarrow 0$ limit of perfect charge correlations in Wigner lattices rationalizes[13] the occurrence of partly-ionic solids, but suppresses the CT absorptions and antiferromagnetic exchange that dominate the optical and magnetic properties. Correlated crystal states retain[3] most of the electrostatic energy of Wigner lattices.

CORRELATED CRYSTAL STATES

We introduce fermion operators $a^{+}_{p\sigma}(a_{p\sigma})$ for creating (annihilating) an electron with spin σ in ϕ_p, the HOMO of D or LUMO of A. The model Hamiltonian referenced to the neutral ...DADA... solid with equivalent A and D sites is

$$\begin{aligned}\mathcal{H} = {} & \sum_{\substack{p>p'\\ \sigma}} t_{pp'}(a^+_{p\sigma}a_{p'\sigma} + a^+_{p'\sigma}a_{p\sigma}) + \sum_{p}^{\text{D sites}}[-\varepsilon_D + U_D(n_p+1)/2](n_p-2) \\ & + \sum_{p}^{\text{A sites}}[-\varepsilon_A + U_A(n_p-1)/2]n_p + \sum_{p>p'} V_{pp'}(n_p-z_p)(n_{p'}-z_{p'})\end{aligned} \qquad (2)$$

Here $n_p = a^+_{p\alpha}a_{p\alpha} + a^+_{p\beta}a_{p\beta}$ is the number operator for site p, the site energies ε_D, ε_A, U_D and U_A are given in Fig. 1, $V_{pp'}$ are Coulomb or other spin-independent intersite interactions, $t_{pp'}$ vanishes except for neighbors in a stack, and $z_D = 2$, $z_A = 0$ are the charges at site p for empty ϕ_p. In 1:1 complexes of N donors and N acceptors there are $N_e = 2N$ electrons and (2) is half filled. Each assignment of N_e electrons to the orbitals $\{\phi_p\}$ may be written[8] as a normalized VB diagram $|k\rangle$ with dots for empty ϕ_p, crosses for doubly-occupied ϕ_p, and lines or arrows for singlets or triplets formed from singly occupied ϕ_p and $\phi_{p'}$. The latter are ion radicals D^+ and A^-. Correlated crystal states ψ_m are linear combinations of $|k\rangle$ with real coefficients that may readily be found for over 10^5 diagrams.[7]

As seen from Fig. 1, $I = \varepsilon_D - U_D$ is the donor's first ionization potential and $A = \varepsilon_A$ is the acceptor's electron affinity. High-energy D^{+2} and A^{-2} sites are excluded[14] from (2) by letting U_A, U_D and $\varepsilon_D \rightarrow \infty$ while keeping $\varepsilon_D - U_D$ constant. This simplification is no longer essential since diagrammatic VB methods readily incorporate all states for arbitrary intersite interactions $V_{pp'}$. The ground state ionicity of a $D^{+q}A^{-q}$ solid is

$$q = \langle\psi_o | n_A | \psi_o\rangle = N^{-1} \sum_{p}^{\text{A sites}} \langle n_p\rangle = 2 - \langle n_D\rangle \qquad (3)$$

The ground-state expectation value of the $V_{pp'}$ terms in (2) yields the correlated Madelung energy per site,

$$M(q) = -\alpha(q)\left|M_1\right| q = \sum_{p\neq 0}\left|V_{po}\right|\langle(n_p-z_p)(n_o-z_o)\rangle \qquad (4)$$

where M_1 is the nearest-neighbor V_{pp+1} for adjacent D^+A^- sites along the stack.

The indicated expectation values of correlated states may be found directly up to N = 12 site fragments,[7] where ψ_0 contains 226,512 singlet VB diagrams. The average ionicity, for instance, does not require larger fragments. Even M(q) in (4) may be accurately estimated[3] via short-range charge correlation functions and the known Wigner-lattice limit of $t \to 0$. The formal development based on one ϕ_p per site consequently shows that correlated crystal states lead naturally to ground-state expectation values. The kinetic energy contribution of (2), which vanishes as $t \to 0$, is now seen to be per site

$$\varepsilon_K(q) = -2\left|t\right| p(q) \qquad (5)$$

where 2p is the bond order, or $\partial\langle\mathcal{H}\rangle/\partial t_{nn}$, and t_{nn} is the nearest-neighbor transfer along the stack.

The t = 0 Wigner lattice contains D^+ and D sites with $n_p = 1$ and 2, respectively, and A^- and A sites with $n_p = 0$ and 1. At q = 1, M(1) is the conventional Madelung energy per site for a singly-ionized lattice $\ldots D^+A^-D^+A^-\ldots$. Simple inorganic salts with cation-anion contacts in the first coordination sphere have $\alpha(q) = \alpha(1)$, since it is energetically favorable to form fully ionized regions. By contrast, partly ionic π-radical solids[3] also have D-D or A-A contacts, as illustrated most simply by the segregated TTF or TCNQ stacks in TTF-TCNQ. TTF-Chloranil or TMPD-TCNQ have planes containing exclusively DA contacts, with D-D or A-A contacts between planes. Now $\alpha(q)$ decreases with increasing q, especially for $q > 1/2$, since less energy is gained per charge on forcing D^+D^+ or A^-A^- contacts. Partly ionic ground states are then readily understood as intermediate phases with lower energy than either the neutral or ionic lattice. Finally, the Hartree-Fock approximation[11] of fractional charges q at each site leads to $\alpha_{HF} = q\alpha(1)$. Now $M_{HF}(q) = M(1)q^2$ is severely reduced around $q = 1/2$ and partly-ionic ground states are excluded.[15] Correlated crystal states lead to $M(q)$ in (4) close to the Wigner lattice when $|t|$ is small compared to the nearest-neighbor Coulomb interactions $|V_{pp'}|$.

In the usual limit of excluding D^{+2} and A^{-2} sites, the ground-state energy per site of (2) becomes

$$\varepsilon_0(q) = (I-A-\alpha(q)|M_1|)q - 2|t|p(q) \qquad (6)$$

on combining (3), (4), and (5). The kinetic energy contribution has been added naturally to the purely potential terms[15,3] with $\alpha(q)$ taken as either the Wigner or HF value. As shown in Fig. 2 for mixed regular rings with on-site interactions, $p(q)$ vanishes near $q = 0$ and becomes small, of the order of $|t|/\Delta E_{CT}$, near $q = 1$. Such results are readily understood qualitatively, since the greatest mixing occurs when $|D^+A^-\rangle$ and $|DA\rangle$ are nearly degenerate. The similar $p(q)$ curves for $N = 6$ and 10 in Fig. 2 illustrate the weak length dependence and the broad maximum around $q \sim 1/2$. The steep initial rise, in particular, shows that a kinetic energy contribution of $|t| \sim 0.2$ ev favors partial ionicity. Similar calculations for Coulomb interactions and lower D^{+2}, A^{-2} energies increase $p(q)$ around $q \sim 1$ to reflect increased CI.

The expectation value of the site terms in (2) give

$$N^{-1}\langle \mathcal{H}_{site}\rangle = q\,(I-A-U_D) - \bar{U}\,(q - \langle q^2\rangle) \qquad (7)$$

with $I = \varepsilon_D - U_D$ as indicated in Fig. 1 and $\bar{U} = (U_A+U_D)/2$. We distinguish carefully between the ionicity $q = \langle n_p\rangle$ and the charge operators whose expectation values are taken in (3). For example, each correlated crystal state has $q_p = 0$ or 1 at every p on excluding D^{+2} and A^{-2} sites; then $\langle q^2\rangle = q$ and the $\bar{U}$ term in (7) vanishes. If we instead (incorrectly) write $q^2 = \langle q^2\rangle$, we obtain exactly the $-\bar{U}q(1-q)$ contribution suggested by Bloch[16] to favor partial ionicity. The present results show that (2) leads to (7) rather than a $-\bar{U}q(1-q)$ term.

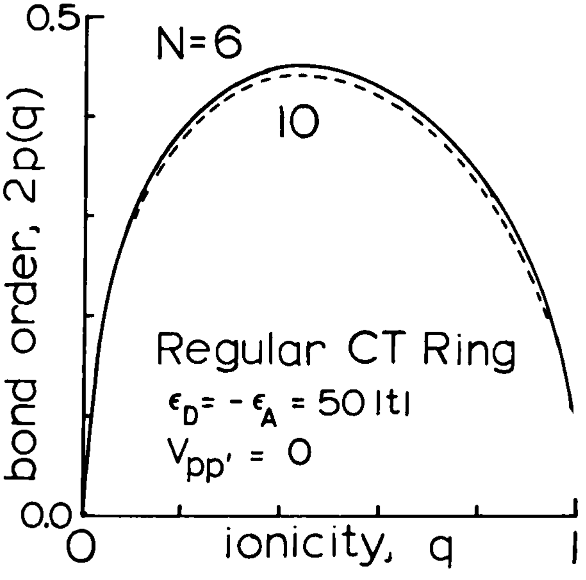

Fig. 2. Kinetic energy per site in regular CT rings with large ε_D, ε_A in (2) to effectively exclude D^{+2} or A^{-2} sites.

CHARGE TRANSFER EXCITATIONS AT INTERMEDIATE IONICITY

The microscopic parameters of the general Hamiltonian (2) are rarely known accurately. Indeed, all single-site relaxation energies may formally be included in ε_D, ε_A, U_A, and U_D, which then merely describe the splittings among ground-state species with different occupancy in ϕ_p. The actual observables are excitation energies like ΔE_{CT} for dipole-allowed transitions, ΔE_p for magnetic excitations above a singlet ground state, or expectations values like the ionicity q in (3) and, less directly, the cohesive energy ε_0 in (6). ΔE_{CT} and q are related in DA dimers[12] as

$$\Delta E_{CT}(q) = \sqrt{2}\,|t|\,[q(1-q)]^{-1/2} = 2[(I-A-|M_1|)^2 + 2t^2]^{1/2} \quad (8)$$

with $0 < q < 1$ on excluding D^{+2} and A^{-2}. The intensity of the CT absorptions in Fig. 3 is indicated by the width of the curve. The dimer results for charge transfer or back charge transfer[11] are symmetric about $q = 1/2$, but no such symmetry occurs in longer fragments or in solids. The general approach of evaluating ΔE_{CT} and ΔE_p at given ionicity q is more useful, in our opinion, than the immediate assignment of all parameters in (2).

The neutral ($q = 0$) ground state is nondegenerate and separated by a gap $\Delta E_p \sim \Delta E_{CT}$ from the lowest triplet. The ionic ($q = 1$) ground state is 2^{2N}-fold degenerate for ion radicals $D^{+}\sigma$ and $A^{-}\sigma$. Finite t for $q \sim 1$ splits[4] the spin states, gives a singlet ground state, and results in antiferromagnetic exchange $J \sim t^2/\Delta E_{CT}$. Since the intensity of dipole transitions vanishes in pure spin states, where no charge redistribution is possible, it follows that back CT in ionic lattices correlates with quite different, higher-energy CT excitations of neutral segments. CT absorptions

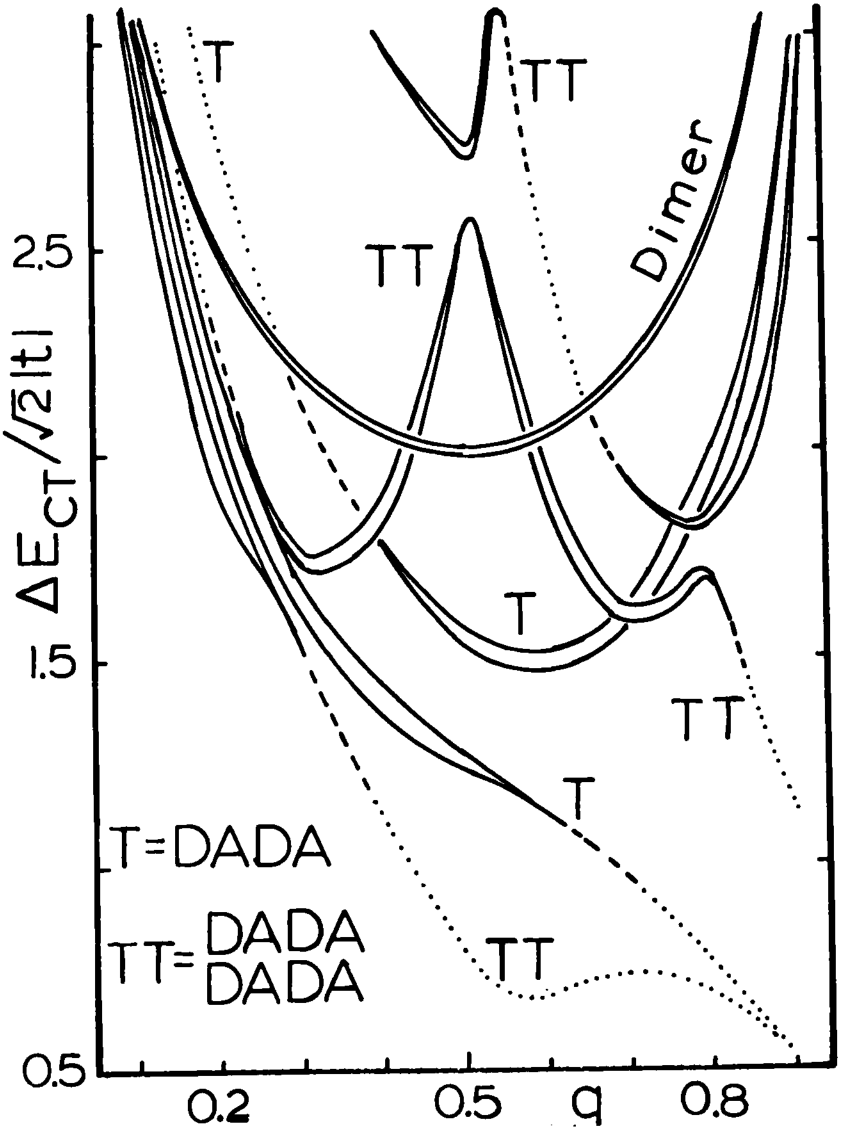

Fig. 3. CT spectra and relative intensities I/N vs. ionicity q for the DA dimer (eq. 8), tetramer (T), and tetramer pair (TT). The absorption width reflects 0.1 < I/N < 0.5; solid lines indicate 0.01 < I/N < 0.1, broken lines 0.001 to 0.01, and dots < 0.001.

and intensities for the linear tetramer in Fig. 3, with just two S = 0 ionic states on excluding D^{+2} or A^{-2} sites, illustrate the different states involved in CT and back CT. As discussed by Bondeson and Soos,[4] CT excitations in longer segments may be approximated by dimers at either $q \sim 0$ or $q \sim 1$, but not in the interesting intermediate regime $q \sim 1/2$ where finite t admixes many configurations.

The TT curves in Fig. 3 represent two tetramers with repulsive Coulomb contacts but no electron transfers ($t_\perp = 0$). For simplicity, we have taken point changes, equal intra- and inter tetramer spacing with $e^2/R = 10|t|$, and have excluded D^{+2} and A^{-2} sites. Around $q = 1/2$, the lowest-energy configuration is a neutral and fully-ionic tetramer that leads to quite different CT spectra. Our illustrative example undoubtedly overestimates interstrand Coulomb interactions, which for planar molecules are closer to second-neighbor intrastack coupling. The point-charge approximation can also be improved[15] by taking delocalized molecular charge distributions. More realistic calculations will also include D^{+2} and A^{-2} sites. We emphasize here that the repulsive interstack contacts which stabilize a partly-ionic ground state also affect the CT spectra. Higher-energy optical transitions of both neutral D or A and ionic D^+ or A^- species may then be expected.

DISCUSSION

Tetramer results underscore the qualitative nature of any dimer model at intermediate ionicities. Similar state and intensity correlations versus q are being found for $N < 8$ segments or $N < 12$ rings on excluding D^{+2} and A^{-2} sites, or in general $N < 10$ rings, whenever symmetry-adapted linear combinations of VB diagrams leads to subspaces of $< 10^3$

basis vectors. Selected excitation energies among low-lying states and all ground state expectation values may be found for 100 times larger bases. Additional work is needed in connection with the proper choice of effective Coulomb potentials $V_{pp'}$ in (2) and of other microscopic parameters. Organic CT solids are far more diverse than conjugated hydrocarbons and there are no "standard" parameters.

Nevertheless, rigorous and practical solutions to quantum cell models like (2) are now available as correlated crystal states. The enormous CI problem in solids reduces to correlation functions among nearby sites. The kinetic energy contribution (5), for instance, is proportional to the bond order in Fig. 2. Intersite Coulomb interactions stabilize $q \sim 1/2$ complexes near the neutral-ionic transition and consequently alter their CT spectra. The higher resolution possible with single-crystal spectra at low temperature and improved probes of molecular vibrations, also demand more complete analyses that incorporate composite CT band, different intensities, intersite Coulomb interactions, and adiabatic electron-phonon coupling.

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