

## CLUSTER APPROACH TO COMPLEX CONDUCTIVITY IN CHARGE TRANSFER CRYSTALS

V.M.Yartsev

Chelyabinsk State University, Chelyabinsk, U.S.S.R.

Low-dimensional organic solids which are characterized by segregated stacks of donor and acceptor molecules often exhibit an arrangement in linear clusters of two, three and four molecules inside the stacks. Reflectance spectra of these compounds show a broad charge transfer (CT) bands polarized along the stacking direction, superimposed by a number of vibronic lines interpreted as a result of electronic coupling to totally symmetric ( $a_g$ ) intramolecular vibrations. The frequency of the CT band has been found to be strongly dependent on the crystal stoichiometry, which indicates the importance of electron-electron correlations.

Eleven years ago Michael Rice has proposed in Dubrovnic [1] that the optical properties of the dimerized compounds may be understood if one considers an isolated dimer of acceptor molecules with two radical electrons which has been transferred from the donors. With the help of linear response theory the problem of the calculation of the complex conductivity and other optical functions has been reduced [1,2] to the following procedure. Firstly, the IR-active antisymmetric linear combinations of  $a_g$  modes are constructed and the part of the Hamiltonian responsible for electron-molecular vibration (EMV) coupling is extracted. Secondly, eigenvalues and eigenfunctions of the electronic subsystem are found in the absence of EMV coupling. Finally, the complex conductivity is calculated as a function of a set of EMV coupling constants.

Since 1978 a number of papers appeared where optical properties of quasi-one-dimensional CT crystals were interpreted by the cluster approach and in most cases the agreement between theory and experimental data was found good enough. In this paper we discuss some recent complex conductivity calculations and pay special attention to the question of the equilibrium charge density distribution among molecules in n-mer and consequent fine structure of vibronic bands.

The microscopic model of EMV coupling is based on the Hamiltonian [1,2]

$$H = H_e + H_v + \sum_{\alpha, i} g_{\alpha i} n_i Q_{\alpha i} - p F, \quad (1)$$

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where  $H_e$  and  $H_v$  describe electronic subsystem and totally symmetric vibrations in the absence of EMV coupling, respectively. Here  $Q_{\alpha i}$  denote the dimensionless normal mode coordinate for the  $\alpha$ -th mode of vibration of  $i$ -th molecule with the frequency  $\omega_{\alpha i}$ . EMV coupling is described explicitly by the third term in (1), where  $n_i$  is the electron number operator for the site  $i$  and  $g_{\alpha i}$  denotes EMV coupling constant. The last term in (1) describes the interaction of  $n$ -meric electronic dipole moment  $p$  with the external electric field  $F$ .

In the framework of the linear response theory the complex conductivity has been obtained for the dimerized [2,3], trimerized (symmetric trimers) [4] and tetramerized [5] compounds. Recently, the cluster of six molecules (two interacting trimers or three dimers) has been considered [6] in order to calculate the influence of interaction between  $n$ -mers on the optical properties.

In the case of arbitrary equilibrium charge density distribution the introduction of symmetric and antisymmetric  $n$ -meric vibrational modes is no longer useful. Instead, as shown in detail elsewhere [7], one can use the linear response theory for several variables [5,6,8]. For a trimer electric dipole moment has the form

$$p = \frac{e}{3} [n_1(-2a-a') + n_2(a-a') + n_3(a+2a')] = \sum p_i n_i, \quad (2)$$

where  $a$  and  $a'$  denote the distances between sites 1-2 and 2-3, respectively. The Hamiltonian (1) can be written in the form

$$H = H_0 + H_{int}, \quad (3)$$

where

$$H_{int} = \sum_i (\sum_{\alpha} g_{\alpha i} Q_{\alpha i} - p_i F) n_i, \quad (4)$$

The Fourier components  $(n_i)_{\omega}$  satisfy the relations

$$(n_i)_{\omega} = \sum_j \chi_{ij}(\omega) [p_j(F)_{\omega} - \sum_{\alpha} g_{\alpha j} (Q_{\alpha j})_{\omega}], \quad (5)$$

$$\chi_{ij}(\omega) = \sum_{\beta} \frac{\langle 1 | n_i | \beta \rangle \langle \beta | n_j | 1 \rangle \cdot 2\omega_{\beta 1}}{\omega_{\beta 1}^2 - \omega^2 - i\omega\gamma_e} = \chi_{ji}(\omega). \quad (6)$$

The Fourier components of normal mode coordinates  $Q_{\alpha i}$  are obtained from (1) in the form

$$(Q_{\alpha j})_{\omega} = - \frac{2g_{\alpha j} \omega_{\alpha j}}{\omega_{\alpha j}^2 - \omega^2 - i\omega\gamma_{\alpha}} (n_j)_{\omega}, \quad (7)$$

From (5) and (7) one can find  $(n_1)_{\omega}$  and consequently complex conductivity

$$\sigma(\omega) = -i\omega \cdot N_t e^2 \frac{\chi_{11}^2 a^2 - 2\chi_{13} a a' + \chi_{33} a'^2 - (\chi_{11}\chi_{33} - \chi_{13}^2) \cdot [a^2 D_3 + a'^2 D_1 + (a+a')^2 D_2]}{1 - \chi_{11} D_1 - \chi_{33} D_3 - (\chi_{11} + 2\chi_{13} + \chi_{33}) D_2 + (\chi_{11}\chi_{33} - \chi_{13}^2) \cdot (D_1 D_2 + D_1 D_3 + D_2 D_3)}$$

where

$$D_i = \sum_{\alpha} \frac{2 g_{\alpha i}^2 \omega_{\alpha i}}{\omega_{\alpha i}^2 - \omega^2 - i\omega\gamma_{\alpha}}$$

and  $\chi_{ij}$  are given by (6). Different  $\omega_{\alpha i}$  automatically lead to the fine structure of vibronic lines.

The same approach of isolated clusters has been used [9] to estimate the activation energy of d.c. conductivity. Examination of various dimerized TCNQ salts have shown that the model of isolated n-mers is able to describe correctly the value of activation energy and the role of electronic correlations if the degree of dimerization is high enough. It looks strange that a regular array of dimers could be described by a model of hopping conductivity generally accepted for disordered systems. The physical reason for this behavior is connected with EMV coupling: the coupling of electrons to numerous intramolecular vibrations plays the same role in destroying the coherent electronic motion as the disorder in amorphous semiconductors.

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