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# ELECTRONIC CORRELATIONS AND ELECTRON-MOLECULAR VIBRATION COUPLING IN PENTAMERIZED CHARGE TRANSFER CRYSTALS

V.M. YARTSEV<sup>a,b</sup> AND C. GARRIGOU-LAGRANGE<sup>b</sup>

<sup>a</sup> Centro de Física, IVIC, Apartado 21827, Caracas 1020-A, Venezuela

<sup>b</sup> Centre de Recherche Paul Pascal, CNRS, 33600 Pessac, France

A cluster approach is used for a theoretical description of the optical properties of pentamerized low-dimensional molecular crystals. Electronic correlations are taken into account explicitly in the Hubbard model for 1, 2, 3, 4 and 5 electrons in a linear pentamer, as well as coupling of electrons to the totally symmetric intramolecular vibrations. Calculated absorbance is compared to the measured one in pentamerized salt of TCNQ and TTF molecules.

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## 1. Introduction

Molecular electronics is generally regarded as a possible way toward further miniaturization of electronic devices down to the characteristic scale of the order of nanometer for modifications of some physical properties. In charge transfer (CT) ion-radical salts, such phenomena as neutral-ionic phase transition, switching and changes in the optical properties under external influences (temperature, pressure, illumination, etc.) have been observed. Hence, these salts, which can be used in the forms of single crystals, powders or Langmuir-Blodgett films, seem to be the most promising materials for molecular electronics. In this respect, it is interesting to understand the factors which govern a degree of localization for physical processes in CT molecular systems. Inspired by the experiments with irradiation of CT molecular crystals [1] which demonstrated that rather small molecular clusters are responsible for optical characteristics, we undertook a systematic study [2] of CT salts where molecules form quasi-isolated clusters of two, three and four entities. The cluster size is determined by the mode of overlap of adjacent molecules: transfer integral between molecules forming a cluster should be much larger than the one between molecules from neighboring clusters. Electronic

correlations, electron-molecular vibration (EMV) coupling and interaction with nearby counter-ions have been shown to be equally important. It is interesting, therefore to investigate relative roles of these interactions as a function of cluster size.

In this paper we present an extension of "dimer" model of Rice [3] to the case of pentamers and discuss the absorption data for recently synthesized pentamerized CT compounds: DPMA<sub>2</sub>(TCNQ)<sub>5</sub> [4] (DPMA = *p*-diphenyl methyl phosphonium-*N,N*-dimethyl aniline) and (TTF)<sub>5</sub>[Pt(CN)<sub>4</sub>]<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub> [5].

## 2. Theoretical model

With the assumption of independent optical responses from different molecular clusters originally used [3] for dimerized ion-radical salts, we consider the Hamiltonian ( $\hbar = 1$ ) of molecular pentamer ABCBA in the form

$$H = H_e + \sum_{i,\alpha} \frac{V_{\alpha i}}{4} (\Pi_{\alpha i}^2 + Q_{\alpha i}^2) + \sum_{i,\alpha} g_{\alpha i} Q_{\alpha i} n_i - \mathbf{p} \cdot \mathbf{E}. \quad (1)$$

We use the extended variant of the Hubbard model [6] in order to take into account the Coulomb repulsion energy,  $V$ , between the electrons on neighboring molecules in addition to the interaction between charge carriers on the same molecule,  $U$ :

$$H_e = \sum_i \Delta_i n_i + \frac{U}{2} \sum_{i,\sigma} n_{i,\sigma} n_{i,-\sigma} + V \sum_i n_i n_{i+1} - \sum_{i,\sigma} t_{i,i+1} (c_{i,\sigma}^+ c_{i+1,\sigma} + c_{i+1,\sigma}^+ c_{i,\sigma}). \quad (2)$$

As usual,  $c_{i\sigma}^+$  ( $c_{i\sigma}$ ) denotes creation (annihilation) operator for the electrons on the site  $i$  with spin  $\sigma = \uparrow, \downarrow$ ,  $n_{i,\sigma} = c_{i\sigma}^+ c_{i\sigma}$ ,  $n_i = n_{i\uparrow} + n_{i\downarrow}$ ;  $t_{ij}$  being the transfer integral between sites  $i$  and  $j$ ;  $t_{AB} = t$ ;  $t_{BC} = t'$ .  $\Delta_i$  describes the  $\pi$ -MO energy shifted with respect to its value in an isolated molecule by the local influence of counter ions increased by the EMV coupling. In Eq. (1),  $Q_{\alpha i}$  denotes the dimensionless coordinate for the  $a_g$  vibration with the frequency  $\nu_{\alpha i}$  of the molecule designated by  $i$ . The strength of EMV coupling is defined by the coupling constants  $g_{\alpha i}$  and  $\mathbf{p}$  denotes the electric dipole moment induced in the molecular cluster by an externally applied field  $\mathbf{E}$ .

In the case of a symmetrical pentamer, we can find two antisymmetric combinations of the modes  $Q_{\alpha i}$  which are active in infrared spectroscopy (three combinations are active in Raman) and the analytic expression for the complex conductivity of pentamerized compounds has the form [7]

$$\sigma(\omega) = -i\omega N \times \quad (3)$$

$$\times \frac{\chi_{11} p_{AA}^2 + 2\chi_{12} p_{AA} p_{BB} + \chi_{22} p_{BB}^2 + (\chi_{12}^2 - \chi_{11}\chi_{22}) (p_{AA}^2 D_B + p_{BB}^2 D_A)}{1 - (\chi_{11} D_A + \chi_{22} D_B) - (\chi_{12}^2 - \chi_{11}\chi_{22}) D_A D_B},$$

where

$$D_A(\omega) = \sum_{\alpha} \frac{g_{\alpha A}^2 \nu_{\alpha A}}{\nu_{\alpha A}^2 - \omega^2 - i\omega\gamma_{\alpha}}, \quad D_B(\omega) = \sum_{\alpha} \frac{g_{\alpha B}^2 \nu_{\alpha B}}{\nu_{\alpha B}^2 - \omega^2 - i\omega\gamma_{\alpha}}, \quad (4)$$

and

$$\begin{aligned}\chi_{11}(\omega) &= \sum_{\beta} \frac{|\langle \beta | n_1 - n_5 | 1 \rangle|^2 2\omega_{\beta 1}}{\omega_{\beta 1}^2 - \omega^2 - i\omega\Gamma}, & \chi_{22}(\omega) &= \sum_{\beta} \frac{|\langle \beta | n_2 - n_4 | 1 \rangle|^2 2\omega_{\beta 1}}{\omega_{\beta 1}^2 - \omega^2 - i\omega\Gamma}, \\ \chi_{12}(\omega) &= \sum_{\beta} \frac{\langle 1 | n_1 - n_5 | \beta \rangle \langle \beta | n_2 - n_4 | 1 \rangle 2\omega_{\beta 1}}{\omega_{\beta 1}^2 - \omega^2 - i\omega\Gamma} = \chi_{21}(\omega)\end{aligned}\quad (5)$$

are the reduced charge transfer electronic polarizabilities in which  $\omega_{\beta 1} = E_{\beta} - E_1$ ,  $E_{\beta}$  and  $\beta$  are the exact eigenvalues and eigenstates of  $H_e$  (2).  $\beta = 1$  labels the ground state. In Eqs. (3) to (5),  $N$  is the number of pentamers per unit volume,  $\Gamma$  and  $\gamma_{\alpha}$  denote the phenomenological widths of the originally uncoupled electronic excitations and vibrational modes, respectively;  $p_{ii} = ea_{ii}/2$ , where  $a_{ii}$  is the intermolecular distance.

In order to calculate the matrix elements (5), it is necessary to find the eigenstates of the electronic Hamiltonian  $H_e$ , defined by Eq. (2). We choose them as linear combinations of the basis states, which include all possible distributions of radical electrons on five sites. The number of these basic states increases rapidly upon the growth of the number of radical electrons per pentamer. Fortunately, we can limit our consideration to the subspace of eigenfunctions of the Hamiltonian (2) with minimal total spin, because the ground state eigenvector belongs to this subspace, as well as all final states accessible via optical excitation. So, we need to solve the systems of 5, 25, 50, 100 and 100 linear equations instead of 10, 45, 120, 210 and 252 generated from Eq. (2) for 1, 2, 3, 4 and 5 electrons, respectively. Then, the matrix elements in Eqs. (5) are calculated and information about allowed optical excitations is obtained explicitly.

### 3. Results and discussion

We calculated absorption spectra for several sets of parameters in the electronic Hamiltonian (2) in the cases of one to five radical electrons per pentamer. Typical spectra are shown in Fig. 1, which clearly demonstrate the effect of electronic correlations. In Table, we present calculated positions of maxima in absorbance. As could be expected, the increase in cluster size leads to the shift of CT band to lower wave numbers (for an isolated dimer the bands are at the energy  $2t$  and  $U/2 + 2t[1 + (U/4t)^2]^{1/2}$  in the cases of one and two electrons, respectively) due to electronic delocalization. The effects of the Coulomb repulsion on neighbouring sites,  $V$ , the mode of molecular overlap resulting in different values of  $t'/t$  and the influence of counter-ions expressed by the parameters  $\Delta_i$  are of the same order of magnitude and none of them can be disregarded. These parameters can be estimated from the structural data.

Theoretical absorbance found from Eqs. (3) to (5) in the cases of two and four electrons per pentamer was used to interpret the experimental data on DPMA<sub>2</sub>-TCNQ<sub>5</sub> [7] (see Fig. 2) and TTF<sub>5</sub>[Pt(CN)<sub>4</sub>]<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub> [4], respectively. These comparisons prove that the cluster approach [3] is valid for molecular aggregates as large as five stacked molecules.

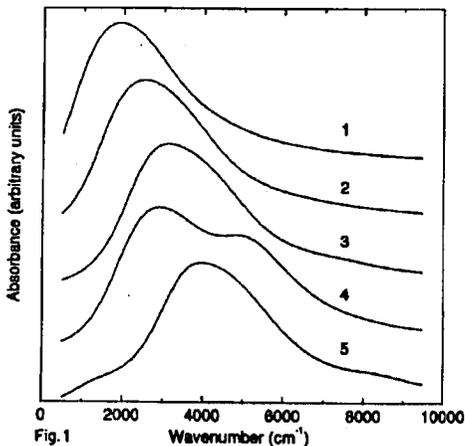


Fig. 1

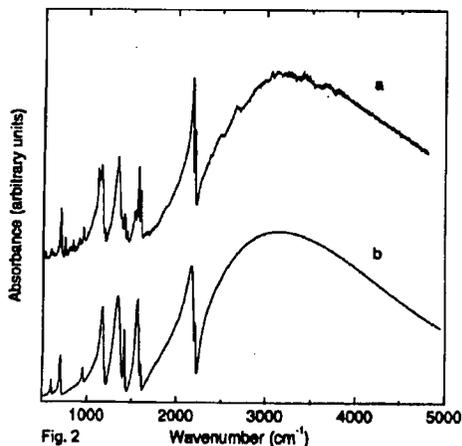


Fig. 2

Fig. 1. Calculated absorbance for different numbers of electrons per pentamer; parameters in Eq. (2) are  $t = t' = 0.2$  eV,  $U = 0.8$  eV,  $V = 0.4$  eV,  $\Delta_A = -0.1$  eV,  $\Delta_B = \Delta_C = 0$ .

Fig. 2. (a) Absorbance of DPMA<sub>2</sub>-TCNQ<sub>5</sub> in KBr pellet at the room temperature. (b) Absorbance calculated with the use of Eqs. (3) to (5).

TABLE

Positions of maxima in absorbance (in  $t$ ) calculated for several sets of parameters in Eq. (2).

| $t'/t$ | $U/4t$ | $V/U$ | $D_A/t$ | $D_B/t$ | $D_C/t$ | Number of electrons per pentamer |      |      |      |      |
|--------|--------|-------|---------|---------|---------|----------------------------------|------|------|------|------|
|        |        |       |         |         |         | 1                                | 2    | 3    | 4    | 5    |
| 1      | 1      | 0     | 0       | 0       | 0       | 1.19                             | 1.46 | 1.59 | 1.55 | 3.12 |
| 1      | 1      | 0.5   | 0       | 0       | 0       | 1.19                             | 1.57 | 1.95 | 1.82 | 2.45 |
| 0.5    | 1      | 0.5   | 0       | 0       | 0       | 0.72                             | 1.65 | 2.60 | 3.28 | 2.95 |
| 1      | 1      | 0.5   | -0.5    | 0       | 0       | 1.09                             | 1.54 | 1.57 | 1.69 | 2.50 |
| 1      | 1      | 0.5   | 0       | -0.5    | 0       | 1.16                             | 1.78 | 1.74 | 2.08 | 2.43 |
| 1      | 1      | 0.5   | 0       | -0.5    | 0.5     | 1.07                             | 1.89 | 1.63 | 2.28 | 2.36 |

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