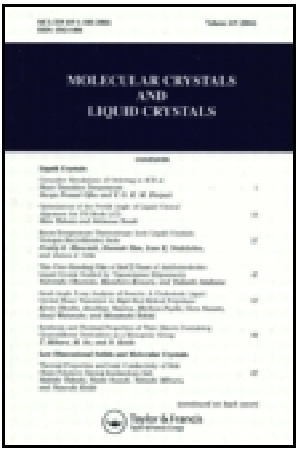

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ELECTRONIC CORRELATION OF ORGANIC CONDUCTORS DETERMINED THROUGH LINEAR AND NON–LINEAR OPTICAL PROPERTIES

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Abstract A 4–site ring model is shown to be a convenient model system to study, on the basis of an Hubbard Hamiltonian, the linear and non–linear optical properties of 1D dimerized half–filled π–conjugated compounds. By using this model one can fit the experimental spectra of representative organic conductors as K–TCNQ and *trans*–polyacetylene. These results show that electronic correlation is important for these materials.

INTRODUCTION

A debate is going on in the literature about the importance of electronic correlation in determining the properties of organic conductors.[1] Charge transfer crystals and conducting polymers are two classes of compounds which belong to this type of materials and the description of their properties has been based on models which do not always take into account electronic correlation. One can recall that properties like the dimerization of the chains which characterizes the crystal structure of many of these organic compounds and their optical gap, particularly of the undoped materials in case of polymers, are directly influenced by electronic correlation, but contrasting points of view have attributed different importance to its effects.[2,3]

Electronic and vibronic excitations of organic conductors can be observed in their linear and non–linear optical spectra and since all these excitations depend on electronic correlation, the fitting of the optical spectra, by a suitable model, makes it possible an evaluation of this type of interaction.

MODEL SYSTEM

Electronic correlation is usually described, for these organic solids, on the basis of an Hubbard model.[3] However the optical properties of an infinite 1D Hubbard model are not known and various type of approximations have been used. The possibility of considering exactly the correlation terms of the Hubbard

Hamiltonian can be obtained by using a Valence Bond approach.[4] In this case the large number of basis functions needed in a calculation limits the number of sites of a model. A small crystal approach allows one to use small rings with periodic boundary conditions to study specific points of the first Brillouin zone of an infinite system.[5]

A 4–site ring model can be used to describe the electronic states at $k = 0$ and at $k = \pi/2d$ of an infinite dimerized chain and therefore it is a convenient model for studying the optical properties of a 1D half–filled system since at these wavevectors one expects a divergent density of states.

OPTICAL PROPERTIES OF K–TCNQ

The 4–site ring model has been recently used to study the electronic and vibronic excitations of the linear spectrum of K–TCNQ, a well known 1D charge transfer compound, as a function of the dimerization of the chain of TCNQ$^-$ radical anions.[6] The vibronic excitations observed in the infrared spectral region are related to the interaction between the totally symmetric intramolecular vibrations of the TCNQ molecule and the charge transfer excitations of a chain. It is well known that the intensity of bands related to vibronic excitations is strongly dependent on the dimerization of the chains and that it vanishes for a vanishing dimerization.[7] The electronic excitations that one can observe in the near infrared spectrum are related to intermolecular charge transfer within the chains. Experiments show that there are two main excitations[8] with that at higher frequency displaying an intensity which again vanishes for the regular system[9] as for the case of the vibronic bands.

The linear optical properties of a 4–site ring model can be obtained by using the velocity operator and the temperature Green's function from which one directly obtains the frequency dependent conductivity.[6] Figure 1 shows the experimental (a) and calculated (b) electronic spectra of K–TCNQ both in the regular and dimerized phases. The values of the parameters of the calculations are reported in Table I.

One notes that the band at about 11000 cm^{-1} is observed and calculated to be present only for the dimerized phases. The small intensity band at about 11500 cm^{-1}, observed for the regular phase, is due to the transition from the lower triplet state. In fact the calculation shows that also this state begins to be populated at 413 K, the temperature at which the spectrum of the regular phase has been recorded. The vibronic bands, not shown in Figure 1, are also calculated correctly and with an intensity which vanishes for the regular phase,

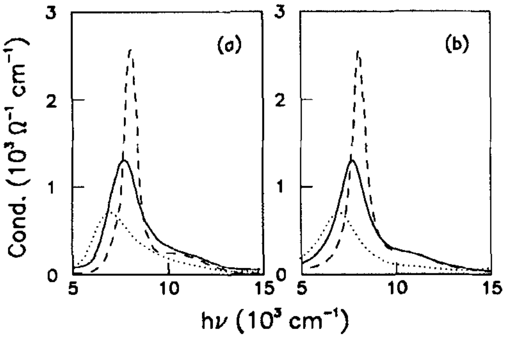

FIGURE 1 Experimental (a) and calculated (b) charge transfer spectra of K–TCNQ. The experimental spectra are redrawn from Ref. 8 and refer to the regular phase at 413 K (dotted line) and to the dimerized phase at 295 K (solid line) and at 27 K (dashed line).

TABLE I Values of the parameters used for the calculations of Fig.1. R refers to the regular phase, D1 to the dimerized phase at room temperature and D2 to the dimerized phase at 27 K. The Hubbard terms U, V_1 and t_i are in eV, the damping constants of the three relevant transitions Γ_{CT_j} are in cm^{-1}. The structural data for (R, D1, D2) are d_1=(3.479, 3.567, 3.580) Å, d_2=(3.479, 3.237, 3.225) Å, density of tetramers=(8.772, 8.929, 8.929)10^{20} cm^{-3}.

	U	V_1	t_1	t_2	Γ_{CT_1}	Γ_{CT_2}	Γ_{CT_3}
R	1.20	0.02	0.19	0.19	1250		1100
D1	1.20	0.28	0.10	0.37	900	1800	
D2	1.20	0.28	0.087	0.383	430	1600	

as experimentally observed. All these spectral features can be accounted for as a function of dimerization since the 4–site ring model takes correctly into account the symmetry of an infinite chain.

From Table I one can see that the values of the parameters which describe electronic interactions are larger than those for hopping integrals. These values show that the system is in an intermediate interaction regime.

OPTICAL PROPERTIES OF POLYACETYLENE

Non–linear optical measurements are not available for K–TCNQ and for charge transfer crystals in general. On the contrary this type of data have been obtained for a representative conducting polymer in its undoped phase such as *trans*–polyacetylene. This polymer can be considered an half–filled dimerized

1D system and therefore it can be described by the same 4–site ring model used above for K–TCNQ. The importance of considering non–linear optical measurements for compounds like polyacetylene and K–TCNQ is that these systems are centrosymmetric and their non–linear optical data may reveal A_g states which cannot be observed in the linear spectra.

The non–linear optical measurement available for *trans*–polyacetylene is the frequency dependent third harmonic generation (THG) below the optical gap.[10] One can observe two bands. The band at lower frequency has been attributed to a 3–photon resonance related to the ^1B_u state which determines the optical gap whereas the second band has been assigned to a 2–photon resonance related to an ^1A_g state.[10]

Models which do not take into account electronic correlation terms[11] and models which consider the last terms but use open chain systems,[12] have found variuos problems in fitting the THG data particularly for what concerns the 2–photon resonance. One can show[13] that both the dimerization, correctly accounted for by a ring system, and electronic correlation are important characteristics that should be considered by a model for the calculation of THG spectra. The third order susceptibility which describes THG spectra, $\chi^{(3)}_{zzzz}(-3\omega;\omega,\omega,\omega)$, can be obtained by using double–sided Feynman diagrams[14] and the velocity operator.

Figure 2 shows the experimental and calculated THG data of *trans*–polyacetylene at room temperature. The values of the parameters used for the calculation are: U=11.26 eV, V_1=5.3 eV, t_1=1.344 eV, t_2=1.856 eV, d_1=1.45 Å, d_2=1.36 Å, density of the tetramers=$1.33\cdot10^{22}$ cm^{-3} and all the damping constants 0.2 eV. One can see that both the 3-photon and the 2–photon bands are satisfactorily accounted for.

A parallel calculation[13] shows that also the linear spectrum can be well reproduced, although in this case, as suggested by theoretical considerations,[15] the overall intensity is overestimated and could be better evaluated by using larger rings than the 4–site one.

The values of the above parameters show that also for *trans*–polyacetylene electronic correlation is important and that this compound is in the intermediate interaction regime as K–TCNQ.

CONCLUSIONS

From the results obtained by the fitting of optical data of two representative 1D half–filled compounds one can see that electronic correlation cannot be

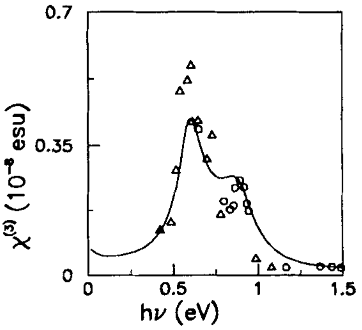

FIGURE 2 Experimental and calculated THG spectra of *trans*-polyacetylene. The experimental data are redrawn from Ref. 10 (△: free electron laser excitation; ○: laser excitation). The calculated THG spectrum is shown as a solid line.

disregarded in describing these materials.

As an example of the importance of taking into account electronic correlation one can suggest an interpretation of the dimerization which characterizes the ground state of these compounds.

The ground state phase diagram of the Extended Hubbard model has been determined, as a function of U/t and V_1/t, on the basis of the 4-site ring model[5] as well as on larger rings.[16] For positive U and V_1 the calculations yield a well known result, namely that a CDW or an SDW regime is expected for $U < 2V_1$ and $U > 2V_1$ respectively. From these data one can see that a system described with values of U and V_1 like those found for K–TCNQ and *trans*-polyacetylene should be in a SDW regime. This situation corresponds to a chain of strongly localized electrons with a large probability of opposite spins on neighboring sites. This spin arrangements resembles that of a strongly dimerized chain. In fact in this case the ground state of the component dimers is a singlet state with opposite spins on the sites. From this observation one can infer that the role of electronic correlation is that of determining a situation of the spin system which favors an instability of the chain toward a dimerized phase in which the energy of the condensed phonon mode is counterbalanced by that of the spin system. The scenario is similar to that of a Spin–Peierls transition but now the spin system results to be freezed in a state which makes possible a transition to a dimerized state already at relative high temperature, contrary to what happens for a pure Spin–Peierls system. From this perspective K–TCNQ and *trans*-polyacetylene resembles Spin–Peierls systems although they are already dimerized at room temperature.

Concluding, one can recall that qualified linear and non-linear optical data, possibly from single crystals, are an important source of experimental data for evaluating many fundamental interactions of organic conductors. From this point of view one observes that non-linear optical spectra of charge transfer crystals, not available at present, are interesting experimental data which could help in understanding the importance of electronic correlation for this type of materials.

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