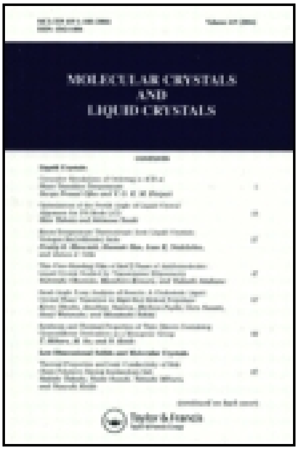

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Electron-Intramolecular Phonon Coupling in regular and Dimerized Mixed Stack Organic Semiconductors

Alberto Girlando [a], Anna Painelli [a] & Cesare Pecile [a]

[a] Inst, of Physical Chemistry, 2 via Loredan, 35131, PADOVA, Italy

Version of record first published: 17 Oct 2011.

To cite this article: Alberto Girlando , Anna Painelli & Cesare Pecile (1985): Electron-Intramolecular Phonon Coupling in regular and Dimerized Mixed Stack Organic Semiconductors, Molecular Crystals and Liquid Crystals, 120:1, 17-26

To link to this article: http://dx.doi.org/10.1080/00268948508075754

Mol. Cryst. Liq. Cryst. 1985, Vol. 120, pp. 17-26
0026-8941/85/1204-0017/$15.00/0

Printed in the United States of America

ELECTRON-INTRAMOLECULAR PHONON COUPLING IN REGULAR AND DIMERIZED MIXED STACK ORGANIC SEMICONDUCTORS

ALBERTO GIRLANDO, ANNA PAINELLI and CESARE PECILE
Inst. of Physical Chemistry, 2 via Loredan,35131 PADOVA,Italy

Abstract A simple model which accounts for the effects of the electron-molecular vibration (e-mv) interaction on the vibrational spectra of regular mixed stack charge-transfer complexes is presented and compared with that working for dimerized mixed stack compounds. The proposed interpretative scheme makes the spectra a powerful source of information on: ionicity; e-mv coupling constants; stack structure; evolution of the phase transitions typical of quasi one dimensional crystals.

INTRODUCTION

Most organic charge transfer (CT) complexes crystallize with the Donor (D) and Acceptor (A) molecules piled alternatively on top of each other to form mixed stacks along which the CT interaction takes place. These compounds are not highly conducting, yet their study brings new insight into one-dimensional physics and its peculiar phenomena. In the present paper we shall be concerned with the role played by the coupling of the CT electron with the intramolecular vibrations of the constituent molecules. The importance of this coupling is well known in the case of segregated stack organic compounds; [1] we shall discuss its consequences on the vibrational spectra of the mixed stack ones, and show how an unified picture of the electron-molecular vibration (e-mv) interaction in segregated and mixed stack crystals can be obtained in terms of the e-mv linear coupling constants, g. [2] We shall also show how the understanding of the perturbative effects of the e-mv coupling on the vibrational spectra allows one to extract detailed information on the structure and properties of quasi one-dimensional CT crystals.

THEORETICAL MODELS

In what follows, we shall always consider the DA chain as isolated and rigid (i.e., we shall disregard the presence of neighbouring chains and of lattice phonons); furthermore, we shall distinguish between two basic types of mixed stack, regular (r-ms) and dimerized (d-ms). In the former, each molecule has the same CT integral with its two neighbours along the chain, whereas in the latter the integrals are different (a fact usually associated with an alternation of the DA distance). CT crystals with d-ms motif are quite rare, but easier to treat theoretically: in fact in this case the rather obvious approximation of disregarding the inter-dimer CT integral in comparison with the intra-dimer one has already led to an exactly solvable model of e-mv interaction.[3] We shall briefly review this model before introducing a first, approximate one relevant to the more difficult problem of a r-ms chain.

In *dimerized mixed stack CT crystals* the DA chain is considered as made up of non-interacting DA pairs. For each pair embedded in the chain the e-mv interaction can be expressed by:[3]

$$H_{e-mv} = \sum_{A} g_A \, n_A \, Q_A + \sum_{D} g_D \, n_D \, Q_D \qquad (1)$$

where n_A and n_D are the electron occupation numbers of A and D molecules, respectively, and the summations are over all the A and D vibrational modes having g's different from zero, i.e. the totally symmetric (ts) ones. This perturbative term is added to the usual electronic and vibrational Hamiltonians of the CT complex; the effect of an externally applied electric field is then treated in the framework of linear response theory. One obtains the following expression for the frequency dependent conductivity:[3]

$$\sigma(\omega) = - i\omega e^2 a^2 N_D \, \chi(\omega) \, / \, \{4(1-\tilde{\chi}(\omega)D(\omega)\} \qquad (2)$$

where $\chi(\omega)$ is the reduced electronic CT polarizability and $\tilde{\chi}(\omega)=\chi(\omega)/\chi(0)$. This expression is the same as that obtained by Rice[4] for dimerized segregated stack (d-ss) insulators. The slight differences in the $D(\omega)$ term (the 1/2 factor and the summation over the modes of both D and A molecules):

$$D_{ms}(\omega) = \tfrac{1}{2}\chi(0) \cdot \sum_{A,D} g^2_{A,D}\, \omega_{A,D} \,/\, (\omega^2_{A,D} - \omega^2 - i\omega\gamma_{A,D}) \qquad (3)$$

can be easily understood by considering that in a radical-radical self-dimer the vibrations of the two molecular units couple each other,[4] whereas this does not happen in a DA complex.[3]

The real part of the conductivity (2) leads to an excitation spectrum analogous to that of a d-ss compound, i.e., a CT excitation and a series of infrared (IR) absorption bands, polarized like the CT one, at frequencies corresponding to those of the Raman (R) ts vibrational modes. In a d-ss system these modes display R lines at frequencies higher than the IR bands, the IR spectrum being the only one affected by the e-mv interaction. In d-ms systems instead, due to the already mentioned lack of coupling between D and A vibrations, the same ts mode is active (obviously with the same frequency) in R and IR, both the spectra being perturbed by e-mv interaction. The frequencies of the e-mv perturbed modes are given by the poles of $\sigma(\omega)$, when regarded as a complex function of a complex variable;[5] by considering only one vibrational mode (i.e., one vibrational band well separated from the others: isolated band approximation), the pole is given by (n=A,D):

$$\Omega_n = \omega_n \sqrt{1-4\, g_n^2\, \rho(1-\rho)\, \omega_n^{-1}\, \omega_{CT}^{-1}} \simeq \omega_n - 2g_n^2\, \rho(1-\rho)\, \omega_{CT}^{-1} \qquad (4)$$

where ω_n and Ω_n are the frequencies of the unperturbed and e-mv perturbed (observed) modes, respectively, ω_{CT} is the frequency of the CT transition, and where the zero-frequency CT polarizability, $\chi(0)$, has been substituted by:

$$\chi(0) = 8\rho(1-\rho)\, \omega_{CT}^{-1} \qquad (5)$$

ρ being the degree of ionicity of the mixed stack compound. It is worth to note that the same approximate expression (4) can be obtained by using simple perturbation theory to calculate the energies of the ground and first vibrationally excited Born-Oppenheimer states.

Eq.(4) shows that the magnitude of the frequency lowering caused by the e-mv coupling is related to g^2, to ω_{CT} and to $\rho(1-\rho)$. The same type of relationship holds for the IR intensity of the e-mv induced bands.[6] From Eqs.(2), (3) and (5) it is also clear that the values of the e-mv coupling constants, g, of both D and A molecules can be extracted from the vibrational spectra of a d-ms compound. The procedure is the following: i) estimate the degree of ionicity, ρ , from the frequencies of the nontotally symmetric modes (the totally symmetric ones are pertubed!); ii) evaluate ω_n from the frequencies of the neutral and fully ionized molecules, assuming a linear dependence from ρ ; iii) solve the set of linear equations (one for each ts mode) corresponding to the poles of $\sigma(\omega)$, considering the g's as the unknowns and introducing the appropiate ω_n, Ω_n, ρ and ω_{CT} parameters. The resulting g values are perhaps less accurate (mainly due to the second step) than those obtainable from the spectra of d-ss compounds,[5] but are easier to exctract since $\chi(0)$ can be evaluated directly from Eq.(5).

Summarizing, on the basis of the above sketched model we can expect the following perturbative effects of the e-mv interaction on vibrational spectra of d-ms CT complexes:

(i) Frequency lowering of the totally symmetric modes;
ii) Appearance of these modes in the IR spectra, with the same polarization of the CT absorption, that is, parallel to the stack axis.

Due to the factor $\chi(0)\propto\rho(1-\rho)$, both these effects will be larger the larger is the difference of from the extreme values 0 and 1: the spectra of compounds with intermediate degree of ionicity will be the most perturbed.

We turn now our attention to the regular mixed stack CT complexes. First of all, we can use simple symmetry arguments to show that the effect of the e-mv interaction on the vibrational spectra is different from the d-ms case. In fact in a r-ms the molecules reside on sites of (at least) C_i, C_2 or C_s symmetry, therefore the ts modes, the only ones affected by e-mv interaction, cannot exhibit IR activity along the stack axis. As a consequence, no e-mv enhanced IR bands are expected for a perfectly regular stack. On the other hand, the R spectra can still be perturbed. In a regular stack each D or A molecule has equal probability of exchanging electrons with the left and right nearby molecules. So we have two degenerate exciton states, and they will combine to give symmetric and antisymmetric parity excited states.[7] Thus, the CT electronic transition takes place between the (symmetric) ground and the antisymmetric excited state. The e-mv interaction, instead, mixes the symmetric exciton states and the ts, R active vibrations of the electronic ground state.

In the r-ms systems we are concerned with, the CT integral is sufficiently large compared to the phonon dispersion energy to consider the electron subsystem faster than the phonon one ("light exciton" case),[8] so that the Born-Oppenheimer approximation can be applied (as already implicitely done in the foregoing discussion) in the description of the electron and phonon states. Thus the e-mv interaction can be again expressed as in eq. (1), with an additional summation to count the unit cells in the chain. However, the solution of the electronic part of the total Hamiltonian is not obvious in the case of a r-ms crystal,[7,9] particularly if one wants to treat compounds with intermediate degree of ionicity. We shall adopt a simple model already used to interpret the optical spectra of r-ms CT crystals.[10] The model singles out a trimeric unit inside the chain; the absorption of the photon is conceived to be a local process, accompanied by the transfer of one electron from the central molecule to the nearest ones. It is quite natural to apply such a local model to our problem, since it is reasonable to think that the vibrations of each D or A molecule are affected only by the CT to the nearest partners; the central molecule of the singled out trimeric unit, on the other hand, keeps the site symmetry it has in a r-ms. The rather drastic approximation of considering the exciton energy independent of wavevector can be partially compensated for by resorting to the experimental frequency of the CT transition (see below).

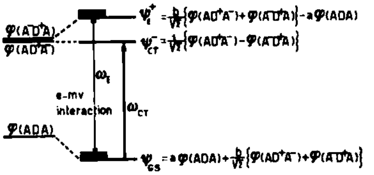

FIG.1 Trimer model:energy levels

In the trimer model the electronic part of the Hamiltonian can be easily solved in the framework of Mulliken's theory, obtaining the energy level diagram shown in Fig. 1. In order to calculate the effect of the e-mv Hamiltonian on the (totally symmetric) vibrational frequencies of the ground state, we apply perturbation theory to the Born-Oppenheimer product wavefunctions $\Psi_E^+ \chi_v$, and $\Psi_{GS} \chi_v$ (χ_v being the usual harmonic vibrational wavefunction). First order perturbation does not affect the energy levels; going to the second order we obtain, in the isolated band approximation, a result analogous to that of d-ms systems, (assuming $\rho=b^2$):

$$\Omega_n \simeq \omega_n - 2g_n^2 \rho(1-\rho) \omega_E^{-1} \tag{6}$$

where ω_E, determined by the energy difference between ground and symmetric excited state, replaces ω_{CT} of Eq.(4). ω_E cannot be measured by simple one-photon spectroscopy, the transition $\Psi_E^+ \leftarrow\!\!-\!\!- \Psi_{GS}$ being allowed only in two-photon processes. Within the limits of the trimer model ω_E is given by:

$$\omega_E = \omega_{CT}(1-\rho)^{-1} \text{ if } \rho < 0.5 \quad ; \quad \omega_E = \omega_{CT}\,\rho^{-1} \text{ if } \rho > 0.5 \qquad (7)$$

Summarizing, on the basis of the above model we expect that the R spectra of r-ms systems will be affected by the e-mv interaction in a way very similar to that predicted for d-ms ones. The ts frequencies will be in fact lowered of an amount related to g^2, to ω_E (rather than to ω_{CT}) and to $\rho(1-\rho)$. The actual dependence on ρ will be different from the d-ms case, but again the frequency lowering will be larger when ρ departs from 0 or 1. Symmetry arguments show that the IR spectra of r-ms compounds are not expected to be influenced by the e-mv perturbation.

COMPARISON WITH EXPERIMENT

The mixed stack CT complex of TTF with Chloranil (CA), the first and so far unique mixed stack complex exhibiting a neutral to ionic phase transition with lowering temperature,[11] constitutes an ideal test system for both the above sketched theoretical models.

Recent X-ray measurements[12] have confirmed that in the low temperature, quasi ionic phase, TTF-CA stack is dimerized. We were indeed able to anticipate this result[3,13] on the basis of the presence of e-mv induced IR bands with polarization along the stack. In fact, as shown above, while the frequency lowering of the ts (a_g) modes can be present in both r-ms and d-ms compounds, their appearance in the IR spectra (at the same frequency of Raman) is an unmistakable sign of stack dimerization. The application of the d-ms model to low temperature TTF-CA yielded the first experimental estimate of TTF and CA coupling constants.[13] The TTF ones nicely compare with those independently determined from the d-ss salt TTF-Br,[5] demonstrating that the g's, as molecular parameters, are indeed transferable between CT crystals of different kind. The validity of the d-ms model has been confirmed also by its capability of reproducing satisfactorily the e-mv induced IR spectrum of low temperature TTF-CA.[13]

The quasi neutral phase[11,13](above 84 K) of TTF-CA can instead be used to test the validity of the r-ms model. In fact, as shown in Fig.2, by lowering the temperature from 300 to 100 K the degree of ionicity of r-ms TTF-CA varies from 0.2 to 0.3. The Fig.2 diagram has been obtained from the frequency of the CA b_{1u} ν_{10} (C=O stretching) vibration, which can be assumed to vary linearly with ρ. A remarkably similar result has been obtained on the basis of the CT transition oscillator strength.[14] Thus, by singling out quasi isolated a_g bands, we can check if their frequency variation with temperature (i.e., with ρ), follows Eq.(6). Fig.3 shows the behaviour of the TTF a_g ν_3 mode (analogous results have been obtained for the CA a_g ν_3). The upper dashed straight line represents the linear dependence of the frequency from ρ , as already tested from the R spectra of ss compounds (triangles).[15] The curved full line on the right (ρ>0.5) represents the behaviour predicted by the d-ms model, with the g_3 adjusted to reproduce the experimental $a_g\nu_3$ frequency of d-ms TTF-CA at 15 K. The full line on the left (ρ<0.5) gives the frequency calculated by the r-ms model (Eq. (6)), with the d-ms g_3 value, ω_E as estimated from Eq.(7) and ω_{CT} and its dependence on temperature taken from Ref.14. The circles are the experimental frequencies taken from the r-ms TTF-CA spectra at various temperatures, the corresponding ρ being estimated from Fig.2. Considering the various approximations done, and in particular the rather rough estimate of ω_E , the agreement between theory and experiment appears quite fair. We can then conclude that in its simplicity the trimer model allows one to grasp the essential physics underlying the effect of e-mv interaction on the vibrational spectra of r-ms CT crystals.

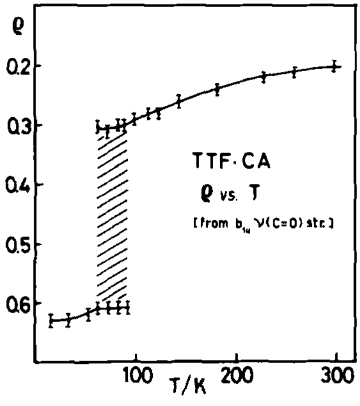

FIG.2 TTF-CA: variation of degree of ionicity with temperature

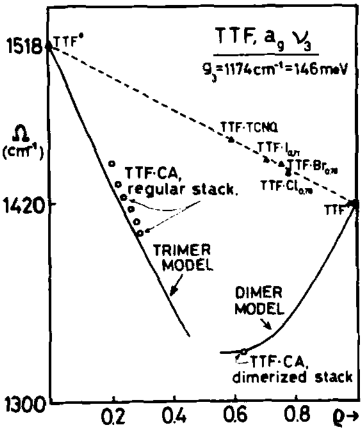

FIG.3 Effect of e-mv interaction

Another important point emerging a dramatic way from Fig.3 is that the (R active) totally symmetric frequencies cannot be used to estimate the degree of ionicity of regular or dimerized mixed stack CT crystals. As a consequence of the e-mv perturbation the linear frequency variation between neutral and fully ionic species is completely lost, while the linear behaviour has been proved to yield reliable estimates of ionicity in the case of segregated stack systems.[1,15]

Although the above interpretative scheme of the e-mv interaction in ms CT crystals has been illustrated here only through TTF-CA, it has been successfully applied in the investigation of several other ms compounds. Table I summarizes the main results, reported in detail in separate papers,[16-20] obtained so far in our laboratory.

TABLE I Ionicity and stack structure of some ms CT crystals

Compound	ρ	Stack type & phase transitions	Ref.
TTF-2,5Cl$_2$BQ	0.2	r-ms	16
DBTTF-TCNQ	0.2	r-ms	16
M$_2$P-TCNQ	0.5	d-ms	18
M$_2$P-TCNQF$_4$	~1	r-ms ← 120 K → d-ms	18
TMPD-TCNQ	0.9	"quasi" r-ms ← 220 K → d-ms	17
TMPD-CA	0.6	d-ms (disordered?)	19
TTF-BA	~1	r-ms ← 55 K → d-ms	20

Here we shall limit ourselves to underline the sensitivity of the IR spectra to the stack dimerization. As we have already seen, the onset of dimerization is marked by the appearance of e-mv induced IR bands, at the same frequency of the R ones and polarized parallel to the stack. This fact can be exploited to follow regular to dimerized stack phase transitions (e.g. M$_2$P-TCNQF$_4$, and TTF-BA in Table I). On the other hand, in the case of TMPD-TCNQ and TMPD-CA such e-mv induced IR bands are present also in the room temperature phase, monitoring a structural situation somewhat different from the r-ms one indicated by the reported X-ray measurements. As explained in detail elsewhere,[17] we suggest that the IR data are indicative of static (defects) or dynamic (fluctuations) stack distortions randomly distributed along the chain.

CONCLUSIONS

In this paper we have summarized an interpretative scheme which accounts for the effects of the e-mv interaction on the vibrational spectra of mixed stack CT crystals. On this basis, the spectra become a powerful investigative tool to probe the physical properties of quasi one dimensional CT crystals. In particular, it is possible to: i) obtain a sufficiently reliable estimate of the degree of ionicity; ii) determine the values of the molecular e-mv coupling constants; iii) study the phase transitions typical of quasi one dimensional crystals: regular to dimerized stack, neutral to ionic ground state; iv) obtain informations about the stack structure [16] and detect possible (static or dynamic) stack distortions.

Acknowledgement - This work has been supported by the National Research Council and by the Ministry of Education of Italy.

REFERENCES

1. R. Bozio and C. Pecile, in The Physics and Chemistry of Low Dimensional Solids, ed. by L. Alcacer (Reidel, Dordrecht, 1980), p. 165.
2. The g's are defined by: $g_n = \partial E_0/\partial Q_n$, where E_0 is the energy of the CT molecular orbital and Q_n the dimensionless n-th normal coordinate (see Ref.5 for details).
3. A. Girlando et al., Phys. Rev., 2306 (1982).
4. M.J. Rice, Sol. State Comm., 31, 93 (1979).
5. A. Painelli, A. Girlando and C. Pecile, Sol. State Comm., submitted.
6. A. Painelli and A. Girlando, unpublished results.
7. D. Haarer, M.R. Philpott and H. Morawitz, J. Chem. Phys., 63, 5238 (1975).
8. E.I. Rashba, in Excitons, ed. by E.I. Rashba and M.D. Sturge (North Holland, Amsterdam, 1982), Chap. 13.
9. D. Haarer and M.R. Philpott, in Spectroscopy and Excitation Dynamics of Condensed Molecular Systems, ed. by V.M. Agranovich and R.M. Hochstrasser (North Holland, Amsterdam, 1983), Chap.2.
10. M. Tanaka, Bull. Chem. Soc. Jpn., 50, 2881 (1977).

11. J.B. Torrance et al., Phys. Rev. Lett., 47, 1747 (1981).
12. Y. Kanai et al., this Conference Proceedings.
13. A. Girlando et al., J. Chem. Phys., 79, 1075 (1983).
14. C.S. Jacobsen and J.B. Torrance, J. Chem. Phys., 78, 112 (1983).
15. S. Matsuzaki, T. Moriyama and K. Toyoda, Sol. State Comm., 34, 857 (1980).
16. A. Girlando, C. Pecile and A. Painelli, J. Physique, C3, 1547 (1983).
17. A. Girlando, A. Painelli and C. Pecile, Mol. Cryst. Liq. Cryst., in press.
18. M. Meneghetti, A. Girlando and C. Pecile, in preparation.
19. A. Girlando, A. Painelli and C. Pecile, in preparation.
20. A. Girlando and J.B. Torrance, unpublished results.