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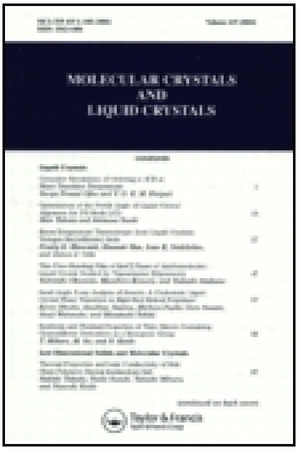

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

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Studies of Organic Semiconductors for 40 Years—V

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Studies of Organic Semiconductors for 40 Years—V

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I. INTRODUCTION

The aim of the present paper is limited to a survey of part of the prolonged research activity of the Padova group in Italy on the structural and electronic properties of organic charge transfer (CT) crystals studied by optical spectroscopy methods. The presentation is given in the form of a short review, without attempting to comprehensively cover all the relevant literature. Attention is focused here on semiconducting CT crystals, but it is worthwhile stressing that optical studies of CT organic conductors and superconductors share many of the concepts, experimental methods and theoretical models discussed here.[1]

In quasi 1D organic semiconductors the generally planar electron donor (D) and acceptor (A) molecules are arranged in stacks, with significant overlap between their frontier orbitals and consequent strong CT interaction along the stack.[2,3] In the following, we shall be mainly concerned with four basic types of stack structure, classified according to their different symmetry. A stack will be named segregated (*s*) if the molecular sites are all equivalent, and mixed (*m*) if two different sites alternate along the chain. The site inequivalence can have two origins: either the molecules making up the stack are different, namely a D and an A molecule, or equal molecules (all D or all A) are differently distorted along the chain. In other words, the distinction between *s* and *m* stacks is made on the basis of the absence or presence of on-site charge density waves (s-CDW). The second classification is on the other hand related to the absence or presence of a CDW between the molecular sites (bond-CDW or b-CDW): in a regular (*r*) stack each molecule has equal CT integrals with its two neighbors along the chain, whereas in a dimerized (*d*) stack the integrals are different. Other, more infrequent stack types (AADDAA stacks, trimerized stacks, etc.)[3] will be explicitly mentioned in due course.

The molecular structure of organic semiconductors (to be contrasted with the atomic structure of conventional inorganic semiconductors) makes the study of the role of molecular vibrations essential and very informative. In fact, due to the presence of low lying (~1 eV) CT transitions (the optical band gap of semiconductor physics), the interaction between CT electrons and molecular vibrations (e-mv coupling) is crucial in determining the physical properties and the peculiar phase

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transitions of these quasi 1-D solids.[4–7] It follows that optical spectroscopy in the region of intramolecular vibrations and CT transitions is a rich source of information on important physical parameters such as the electron-phonon coupling constants, the degree of ionicity, the CT integral, and the on-site interelectronic correlation energy. Moreover, from the structural point of view one can throw light on the type of stack (mixed or segregated, regular or distorted) and characterize the temperature and pressure induced phase transitions.

A fundamental prerequisite for the investigations on organic semiconductors outlined above is knowledge of the vibrational behavior of the molecular constituents and of the corresponding radical ions. The achievement of this basic step is rather complex and lengthy; some of the specific difficulties are described in a preceding review[4] and will not be considered here. We shall only mention that a sufficiently sound knowledge of the vibrational behavior has been reached, for example, for the following key D and A molecules: tetrathiafulvalene (TTF)[8] and its various derivatives (dibenzo-TTF, DBTTF[9]; tetramethyl-TTF, TMTTF, and its Se analog, TMTSF[10]); tetramethylparaphenylendiamine (TMPD)[11]; tetracyanoquinodimethane (TCNQ)[12] and its fully fluorurated analog ($TCNQF_4$)[13]; the family of the haloquinones, and in particular the chloranil (CA) and bromanil (BA) structures.[14]

II. MODEL HAMILTONIAN

The electronic structure of a quasi 1D CT crystal is generally described by a tight-binding hamiltonian, i.e., in terms of weakly interacting molecular site orbitals.[2] Such molecular site wavefunctions can in turn be expressed as products of an electronic and a vibrational part, the former being referred to a fixed nuclear configuration ("crude adiabatic representation").[5] Due to the high anisotropy of the system, the overlap between the molecular orbitals on adjacent stacks is negligible, and the only important interstack interaction is the Coulomb one. Thus the problem can be reduced to that of a single stack, the relevant parameters being renormalized through a mean field treatment of the interstack interaction. Finally, if one explicitly accounts only for the frontier molecular orbitals and neglects the overlap between the orbitals on non-nearest neighbor sites, the electronic hamiltonian for the system reduces to the well known extended Hubbard hamiltonian:[15]

$$H_e = \sum_{i,\sigma}\epsilon_i a^+_{i,\sigma}a_{i\sigma} + \sum_{i,\sigma}t_i(a^+_{i,\sigma}a_{i+1,\sigma} + \mathrm{H.c.}) + \frac{1}{2}\left\{\sum_i U_i\hat{n}_i(\hat{n}_i - 1) + \sum_{ij}{}' V_{ij}\hat{\rho}_i\hat{\rho}_j\right\} \quad (1)$$

where i runs on the N molecular sites of the stack, and σ runs on the spin indexes α, β. $a^+_{i,\sigma}$ ($a_{i,\sigma}$) are the fermion creation (annihilation) operators for an electron with spin σ on the i-th site, $\hat{n}_i = \sum_\sigma a^+_{i,\sigma}a_{i,\sigma}$ is the number operator which counts electrons on the i-th site and $\hat{\rho}_i$ is the site charge operator defined as $\hat{\rho}_i = 2 - \hat{n}_i$ for D sites, $\hat{\rho}_i = -\hat{n}_i$ for A sites. Finally, in Equation (1) ε_i is the i-th site energy, t_i the CT integral between i and $i + 1$ sites, U_i the on-site interelectronic (Hubbard) repulsion energy, whereas V_{ij} represents the repulsion energy between charges on i and j sites.

In dealing with the vibrational hamiltonian, one generally concentrates on the zone-center phonons, the only ones optically active. Furthermore, the three dimensional structure of the phonons is neglected. We choose the same reference state as for the electronic hamiltonian, i.e., the vacuum state, a collection of non-interacting D^{2+} and/or A molecules. In terms of the corresponding dimensional (spectroscopic) normal coordinates,[5] R, and frequencies (ω) the vibrational hamiltonian in the harmonic approximation reads (here and henceforth $\hbar = 1$):

$$H_\nu = \frac{1}{2} \sum_{\mu} (\dot{R}_{v,\mu} + \omega^2_{v,\mu} R^2_{v,\mu}) \tag{2}$$

where μ runs on the crystal normal modes and the v index refers to the vacuum state. Since we are dealing with molecular crystals, it is convenient to distinguish between molecular and lattice phonons. The former are linear combinations of the vibrational modes of the isolated molecules, and have approximately the same frequency, whereas the latter are combinations of the molecular translations and rotations.

Having described the "crude adiabatic" electronic and vibrational hamiltonians, the electron-phonon interaction hamiltonian (H_{ep}) can be introduced by expanding H_e on the vibrational coordinates. Consistently with the harmonic approximation, the expansion is carried out to the second order:

$$H_{ep} = \sum_{\mu} \left(\frac{\partial H_e}{\partial R_{v,\mu}}\right)_v R_{v,\mu} + \frac{1}{2} \sum_{\mu,\mu'} \left(\frac{\partial^2 H_e}{\partial R_{v,\mu} \partial R_{v,\mu}{'}}\right) R_{v,\mu} R_{v,\mu}{'} \tag{3}$$

where v again indicates the vacuum state. Both on-site energies and bond energies can be modulated by the crystal vibrational modes. Since only molecular vibrations are able to modulate on-site energies, whereas bond energies are mainly modulated by lattice phonons,[5] the two kinds of coupling are usually referred to as electron-molecular vibration (e-mv) and electron-lattice phonon (e-lph) couplings. We shall now briefly discuss them in turn, by substituting R_μ by Q_γ or U_ν, to distinguish between e-mv and e-lph coupled normal coordinates respectively.

Of the two on-site terms of Equation (1), ϵ_i and U_i, only the former can be considered to be appreciably modulated by the Q's, so that Equation (3) yields the following terms:

$$\left(\frac{\partial \epsilon_i}{\partial Q_{i,\gamma}}\right)_v = \tilde{\omega}_\gamma \, I_{i,\gamma} = \sqrt{2\omega_{v,\gamma}} \, g_{i,\gamma} \tag{4}$$

$$\left(\frac{\partial^2 \epsilon_i}{\partial Q^2_{i,\gamma}}\right) = \tilde{\omega}^2_\gamma - \omega^2_{v,\gamma} - \left(\frac{\partial^2 \epsilon_i}{\partial Q_{i,\gamma} \, \partial Q_{i,\gamma'}}\right) = 0 \tag{5}$$

where the γ index runs on the molecular normal coordinates, and i on the lattice sites, whereas $\omega_{v,\gamma}$ ($\tilde{\omega}_\gamma$) is the vibrational frequency of the γ-the mode in the vacuum (mono-occupied) state, and $I_{i,\gamma}$ is the difference between the equilibrium values of $Q_{i,\gamma}$ for the i-th molecule in the mono-occupied and vacuum state. Equation (4) defines the basic parameters of the theory, the e-mv (linear) coupling constants, $g_{i,\gamma}$, whereas Equation (5) holds in the hypothesis that the $Q_{i,\gamma}$ modes are not appreciably changed (mixed) by changing the oxidation state of the i-th molecule. In this hypothesis the second order coupling constant $(\bar{\omega}_\gamma^2 - \omega_{v,\gamma}^2)$ does not depend on where the derivative is evaluated, whereas the $g_{i,\gamma}$ does. It has been found[5] that the linear e-mv coupling constants depend on the average charge on the molecule:

$$g_{i,\gamma}(\rho) = \left[\frac{\omega_{v,\gamma}\bar{\omega}_\gamma}{\omega_\gamma^2(\rho)}\right]^{5/4} \quad [g_{i,\gamma}(0)g_{i,\gamma}(1)]^{1/2} \tag{6}$$

where $\rho = |\langle\rho_i\rangle|$, and $\omega_\gamma(\rho)$, $g_{i,\gamma}(\rho)$ are the vibrational frequency and e-mv coupling constant for i-th molecule with ionicity ρ. While second order e-mv coupling constants are in general finite quantities for all the molecular modes,[5] and are easily evaluated from the experimental frequencies of neutral and fully ionic molecules,[4] it is important to keep in mind that for non-degenerate electronic orbitals the linear e-mv coupling constants are different from zero only for totally symmetric, ts (in the molecular point group), molecular vibrations.[16]

From Equations 4–6 it is evident that the linear and quadratic e-mv coupling constants are molecular parameters, and as such can be transferred between different crystals with different structures and microscopic and/or macroscopic properties, provided they are made up of the same molecular units. This is the feature which makes the investigation of the effects of e-mv coupling on the optical spectra so useful in analysing and understanding the properties of organic semiconductors.

Turning our attention to the e-lph coupling, we define the following linear e-lph coupling constant:

$$g_{i,\nu} = (2/\omega_\nu)^{1/2}\,(2/N)^{-1/2}\,(\partial t_i/\partial U_\nu) \tag{7}$$

Actually U_ν modes can also modulate V_{ij}, but it has been shown[7b] that the resulting first order coupling vanishes for regular chains and is expected to be negligible for not strongly distorted chains. The second order coupling could of course be introduced through the second order derivative of the t_i's and V_{ij}'s on the U's. In any case the e-lph coupling constants depend essentially on the crystal lattice parameters, and cannot be reduced to molecular properties. The consequent non-transferability of the e-lph coupling constants makes the investigation of their effects on the optical spectra of organic semiconductors more difficult and also less useful than the investigation of the e-mv coupling. This is the reason why, although such effects can be theoretically predicted (see next Section), they have not so far been experimentally investigated.

III. EFFECTS OF ELECTRON-PHONON COUPLING ON THE OPTICAL SPECTRA OF ORGANIC SEMICONDUCTORS

Electron-phonon coupling plays a foundamental role in determining many basic properties of solids, such as finite resistance of metals, BCS superconductivity, structural phase transitions such as Peierls' in quasi 1D crystals, and so on. As already stated in the Introduction, in this paper we limit our attention to a particular aspect, namely, the effects that electron-phonon coupling produces on the vibrational spectra of quasi 1D organic semiconductors. From this point of view, it is convenient to consider the lattice as already relaxed to its equilibrium position, so that the electronic structure is not strongly affected by electron-phonon coupling. In these conditions we can introduce H_{ep} as a perturbation on the "crude adiabatic" solution of $H_e + H_v$.

As already anticipated in the preceding Sections, the solution of H_v can be obtained, at least for molecular phonons, from the interpretation of the vibrational spectra of the constituent molecules in different oxidation states.[4,8-14] The solution of H_e, on the other hand, is in general a rather difficult task. Analytical solutions of Equation 1 hamiltonian for an infinite stack cannot be found, as one would have to start with a very large (actually infinite) number of basis functions. One type of approximation often used to reduce the basis set has been to break the chain into smaller, non-interacting units, disregarding the CT integrals between the units themselves. For instance, a *d* chain can be modeled by a collection of dimers,[17,18] a trimerized one as a collection of trimers, and so on. The second type of approximation consists in disregarding the highest energy wavefunctions, and has been used to investigate the effect of interdimer[5] and intertrimer[19] CT interaction in *d* and trimerized stack systems. Neither kind of approximation is really adequate to describe the properties of *r* stacks,[5] and for these systems numerical methods are generally preferred.[6,7] On the other hand, even if the adopted solution for H_e is quite rough, it suffices to achieve a good description of the effects of electron-phonon coupling on the vibrational spectra. This point will be illustrated in Section V through an experimental example, and will show that a properly chosen semi-empirical approach to the solution of H_e is generally adequate.

Several methods, perturbative and non-perturbative, have been proposed to account for the introduction of H_{ep} in the "crude adiabatic" solution of $H_e + H_v$. The methods and their merits have been extensively discussed in a recent paper[5] which presents the basic theoretical framework of e-mv coupling in CT crystals, and to which we refer for details. This paper shows that the so called VAM approach (vibronic adiabatic Mulliken theory) is the most suitable to deal with quadratic electron-phonon coupling. It turns out that this coupling can be accounted for by renormalizing the vibrational frequencies and linear electron-phonon coupling constants from the values relevant to the vacuum state to those relevant to the actual charge distribution for the crystal in its equilibrium state. This very useful result can be understood, in physical terms, by observing that in the harmonic approximation the second order electron-phonon coupling cannot mix the electronic ground to excited CT states; its effects can therefore be introduced by renormalizing the ground state vibrational parameters.

As a consequence, the interesting physics of electron-phonon coupling is associated with the linear term, which is able to mix ground and excited states, giving rise to peculiar vibronic phenomena in the optical spectra. Therefore, with the only proviso that ω_μ, g_μ and R_μ are properly renormalized, the H_{ep} hamiltonian in Equation (3) can be reduced to the linear term. In these conditions, equivalent solutions to the problem can be obtained either by the VAM method[5] or by linear response (LR) theory.[17,18] We shall follow the former scheme as, in our opinion, it offers a more immediate understanding of the underlying physics.

Among the four basic types of stacks mentioned in the Introduction (*rs*, *rm*, *ds*, *dm*), the *rs* stack type is trivial, since the zone-center phonons are not coupled to electrons, and no effect of electron-phonon coupling is expected either in infrared (IR) or in Raman. For the other three types of stack the linear H_{ep} hamiltonian can be written as:

$$H_{ep} = \vartheta_\nu \sum_\gamma \sqrt{\omega_\gamma} g_\gamma Q_\gamma + \vartheta_b \sum_\nu \sqrt{\omega_\nu} g_\gamma U_\nu \tag{10}$$

where ϑ_ν and ϑ_b are purely electronic operators, whose form for the different stacks can be found in Reference 5. By perturbatively expanding the ground state total (electronic + vibrational) energy up to the second order in H_{ep}, and then evaluating its second derivatives on the normal coordinates, one finds the force constants matrix (**F**) of the system, whose elements are:

$$F_{\mu\mu'} = \omega_\mu^2 \, \delta_{\mu\mu'} - 2\sqrt{\omega_\mu \omega_{\mu'}} \, g_\mu g_{\mu'} \chi \tag{11}$$

where $\omega_\mu \equiv \omega_\mu(\rho)$ and $g_\mu \equiv g_\mu(\rho)$ and χ is the electronic response to the perturbation induced by R_μ and $R_{\mu'}$:

$$\chi = \sum_F \langle G|\vartheta|F\rangle\langle F|\vartheta'|G\rangle/\omega_F \tag{12}$$

where $\vartheta(\vartheta') = \vartheta_\nu$ if $R_\mu \equiv Q_\gamma$ and $\vartheta(\vartheta') = \vartheta_b$ if $R_\mu \equiv U_\nu$, whereas ω_F is the frequency difference between ground $|G\rangle$ and excited $|F\rangle$ electronic CT states.

The diagonalization of the **F** matrix gives the electron phonon perturbed frequencies of the system, i.e., the experimental ones, which turn out to be generally lowered in respect to the unperturbed frequencies. Of course, the normal coordinates also change, becoming linear combinations of the original R_μ, mixed by their common interaction with the CT excited states. This interaction also gives rise to a perturbation of the intensities of the vibrational modes: for instance in IR the electron phonon coupled modes can borrow intensity from the nearby CT excitations. In fact one can use the ground state electronic wavefunction, corrected to the first order in H_{ep}, to evaluate the ground state electric dipole moment. Its first derivative in respect to R_μ gives the transition dipole moment, $\mathcal{M}_\mu$, of the corresponding vibration:

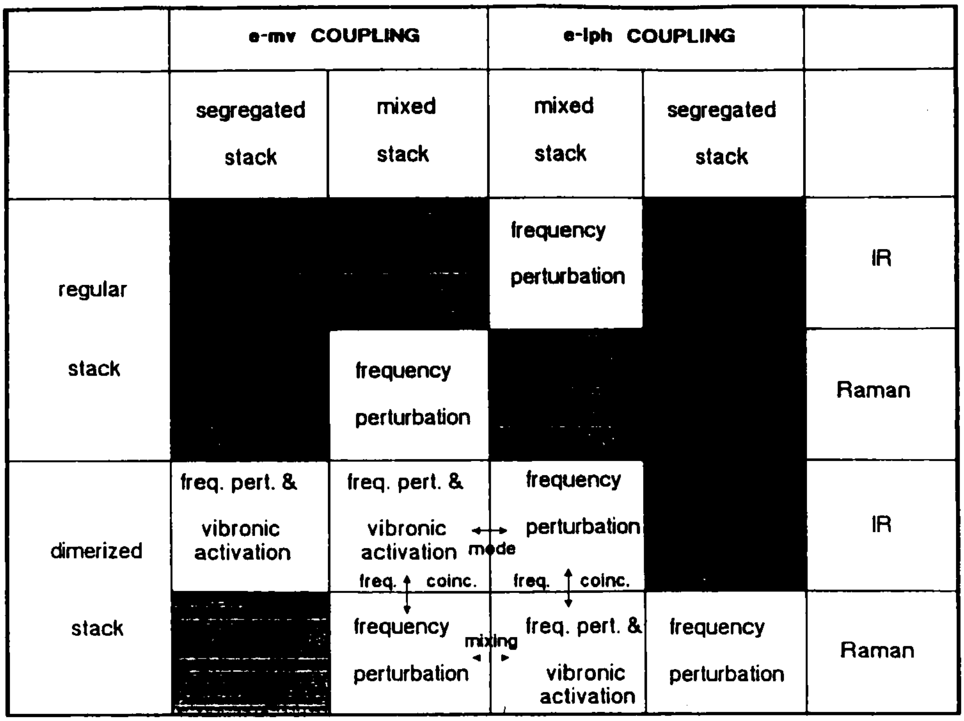
$$\mathcal{M}_\mu = 2\sqrt{\omega_\mu} \, g_\mu \sum_F \langle G|\mathcal{M}|F\rangle\langle F|\vartheta|G\rangle/\omega_F \tag{13}$$

where $\mathcal{M}$ is the dipole moment operator and again ϑ indicates either ϑ_ν or ϑ_b. Once the frequency, shape and transition dipole moment of the electron phonon coupled modes are known, one has an essentially complete description of the IR excitation spectrum of the system and has enough information to simulate the electron-phonon induced experimental spectrum, in terms, for instance, of the frequency dependent conductivity, $\sigma(\omega)$. Explicit expressions of $\sigma(\omega)$ are found in Reference 5, and an example of spectral simulation will be reported in Section V. The LR approach[17,18] leads to equivalent results, yielding an expression for $\sigma(\omega)$ more directly. The electron-phonon perturbed frequencies are given by the poles of $\sigma(\omega)$ and correspond to those obtainable by diagonalizing of the VAM **F** matrix. In addition, we remark that with a calculation analogous to that used for $\mathcal{M}_\mu$, one could also derive information on the electron-phonon perturbed Raman intensities of the R_μ modes through the first derivatives of the ground state polarizability.

So far we have described a fairly general treatment of electron phonon coupling in organic semiconductors, without specializing it for a particular stack type. Very simple symmetry arguments are sufficient to understand that the effect of the electron-phonon coupling on the vibrational spectra is different for different stack types.[5,9,18,20] In fact it is obvious from Equations 3 and 10 that ϑ_v and ϑ_b operators have the same symmetry as the Q_γ and U_ν modes, respectively. Now, in systems where just one CDW is present, either a s-CDW (*rm* stack) or a b-CDW (*ds* stack), one symmetry element along the chain is retained, namely an inversion center[21] lying respectively on the molecular sites or between them. In both cases Q_γ and U_ν (i.e., ϑ_v and ϑ_b) belong to different symmetry representations and cannot be mixed by electron-phonon interaction: the **F** matrix of Equation (11) is block diagonal. The mutual exclusion rule[22] holds, and Q_γ (U_ν) modes cannot appear contemporaneously in IR and Raman. Moreover, Equation (13) indicates that in *rm* stacks the U_ν modes, and in *ds* stacks the Q_γ ones, borrow IR intensity from the nearby CT transition. This result is particularly important for *ds* stacks, since for such systems the predictions of the oriented gas model,[23] usually adopted in dealing with optical spectra of molecular crystals, are not obeyed: strong bands, polarized along the stack axis, and corresponding to ts modes (the only ones with $g_\gamma \neq 0$)[16] appear in IR, whereas the oriented gas model would predict zero intensity. This breakdown of the oriented gas model has often been referred to as a "vibronic activation" of the ts modes in the IR spectra.[4]

In *dm* stack systems the absence of symmetry elements along the chain makes both Q_γ and U_ν modes contemporaneously active at coincident frequencies in IR and Raman.[18] Vibronic activation occurs only for Q_γ in the IR spectra and for U_ν in the Raman ones. For sake of completeness one should note that the lack of symmetry allows the mixing of Q_γ and U_ν modes through their common interaction with CT electrons, and consequent intensity redistribution and frequency changes. However, such mixing is expected to be slight due to the generally large frequency separation between Q_γ and U_ν modes.[5,24]

Figure 1 summarizes the above discussed effects of electron-phonon coupling in organic semiconductors of different stack type. Only four basic types of stacks have been considered, but the extension of the above arguments to other stack structures is straightforward.[19] Figure 1 reports the theoretical "selection rules" for both e-lph and e-mv couplings, but since only the effect due to e-mv coupling have been widely experimentally studied, we shall henceforth restrict our attention to the latter.



	e-mv COUPLING		e-lph COUPLING		
	segregated stack	mixed stack	mixed stack	segregated stack	
regular stack	■	■	frequency perturbation	■	IR
	■	frequency perturbation	■	■	Raman
dimerized stack	freq. pert. & vibronic activation	freq. pert. & vibronic activation	frequency perturbation	■	IR
	■	frequency perturbation	freq. pert. & vibronic activation	frequency perturbation	Raman

FIGURE 1 Effect of electron-phonon coupling on the vibrational spectra of organic semiconductors.

IV. MICROSCOPIC PARAMETERS FROM OPTICAL SPECTRA

In this Section we shall describe how optical data allow one to estimate several microscopic parameters characterizing the CT electronic structure and the strength of e-mv interaction in organic semiconductors. From the excitation spectrum in the CT region one determines the energy of the CT transition(s) and the corresponding oscillator strength (f_{CT}). The latter information is best obtained through polarized absolute reflectivity data on single crystals,[25] although in favorable cases absorption spectra of powdered samples can also be employed.[26] From these data, one can extract the microscopic parameters relevant to the model adopted to describe the electronic structure of the system. For instance, if a *ds* stack can be regarded as a collection of non-interacting Hubbard dimers, the effective (renormalized) t and U can be estimated from ω_{CT} and f_{CT}.[17,25] Some examples are reported in the upper part of Table I. In *m* stack CT crystals the CT electronic structure is generally characterized by t and ρ, the degree of ionicity, which reflects the mixing between D and A orbitals.[2,7,27] These two parameters can be obtained from ω_{CT} and f_{CT}, either by using the dimer model[27] (*dm* stack) or through many-body calculations[6] (*rm* stack). However, the ionicity of CT crystals is more directly and precisely estimated *via* vibrational data, as we are going to describe. Therefore, in *m* stack systems one generally determines ω_{CT} from the CT excitation spectrum,

TABLE I

Microscopic parameters of organic semiconductors derived from optical spectra.

Compound[a]	Stack	Ionicity (ρ)	|t|/eV	U/eV	Ref.
K TCNQ	ds	1.0	0.31	0.51	5
MEM $(TCNQ)_2$	ds	0.5	0.20	—	17b
DMeFc(TCNQ)	isolat. dimers	1.0	0.27	1.00	25
TTF Br	" "	1.0	0.31	1.35	this work
				Z/eV	
HMB TCNQ	rm	0.1	0.30	−0.68	6
BD TCNQ	rm	0.2	0.28	−0.32	6
TTF $2{,}5Cl_2BQ$	rm	0.2	0.30	−0.34	9,this work
DBTTF-TCNQ	rm	0.2	0.25	−0.28	9,this work
TTF CA	rm	0.2	0.21	−0.24	6
TTF CA, 45K	dm	0.6	0.22	0.06	29,this work
M_2P TCNQ	dm	0.5	0.22	0.00	37,this work
TMPD CA	dm	0.6	0.31	0.09	38,this work
TMPD TCNQ	quasi-rm	0.9	0.18	0.41	11,this work
TTF BA	rm	1.0	0.14	0.44	43,this work

[a] MEM: Methylethylmorpholinium; DMeFc: Decamethylferrocenium; HMB: Hexamethylbenzene; BD: Benzidine; $2{,}5Cl_2BQ$: 2,5-Dichloro-p-benzoquinone; M_2P: Dimethylphenazine.

and ρ from vibrational data. From these quantities and a proper model[7,27] it is straightforward to extract *t* and *Z*, half the energy required to destroy an ionic pair embedded in a lattice with charge ρ.[28] This quantity plays a role analogous to that of *U* for *s* stacks, and defines the neutral-ionic (N-I) borderline for *m* stack CT crystals.[7,27] The microscopic parameters of a number of *m* stack systems are shown in the lower part of Table I.

In the absence of first order e-mv coupling, either because the *g*'s are zero (non-ts modes) or due to the symmetry of the chain, the use of vibrational spectroscopy to determine the ionicity of the system is straightforward. In fact, within the approximations of the e-mv model described in the previous Sections (in particular, no normal mode mixing upon ionization) it can be shown[5] that the second order e-mv coupling yields the following expression for frequency ω_γ of the γ-th vibrational model of a molecule with charge ρ:

$$\omega_\gamma = [\omega^2_{v,\mu} - \rho(\omega 2_{v,\gamma} - \tilde{\omega}^2_\gamma)]^{1/2} \simeq \omega^0_\gamma - \Delta_\gamma \rho \tag{14}$$

where ω^0_γ is the frequency of the neutral molecule and Δ_γ is the ionization frequency shift. Thus, the frequency of the molecular vibrations is related in a simple, direct way to the charge density on the molecular site. Of course, the charge density is the one experienced by the molecular vibrations, i.e., ρ is estimated in the vibrational time scale, $10^{-13} - 10^{-14}$s. The above linear relationship has been experimentally tested and found to give rather accurate estimates of ρ, provided Δ_γ is large enough (>20–25 cm^{-1}).[4,29]

The first order e-mv coupling alters the above picture dramatically. If, for the sake of comparison with Equation (14), we disregard the interaction between the modes caused by their coupling with the CT electron (isolated band approximation),[20,29] from Equation (11) one derives the following expression for the frequency, Ω_γ, of the γ-th e-mv perturbed mode:

$$\Omega_\gamma^2 = \omega_\gamma^2 - 2\omega_\gamma g_\gamma^2 \chi_\nu \tag{15}$$

where χ_ν is the electronic response to the perturbation induced by the molecular vibrations. Equation (15) shows that the frequency of a ts mode may exhibit significant departures from the linear behavior of Equation (14). Therefore, before the frequency of a ts mode is used to estimate ρ, one must be aware of the possible interference of the linear e-mv coupling. This fact has often been overlooked, in particular for what concerns the Raman ts frequencies of *rm* stack compounds (cf. Figure 1, left side). As an example, in Figure 2 we report the behavior of the TTF a_g ν_3 mode in different CT crystals. In *s* stacks, where first order e-mv coupling is absent, the frequency exhibits a linear dependence on ρ (dashed line). On the other hand for an *m* stack CT crystal, TTF-CA, which has a neutral regular stack above 84 K and an ionized dimerized one below,[29] Equation (15) is followed (continuous line, left and right side, respectively). Notice that since χ_ν for an *m* stack (either *r* or *d*) vanishes for $\rho \rightarrow 0$ and $\rho \rightarrow 1$, the perturbing effect tends to disappear in the same limits.[6,20]

From the above discussion one deduces that the use of the ts modes should be avoided in the estimation of ρ, unless one is able to precisely take into account the effect of e-mv perturbation. In fact, Equation (2) shows that, if the g's are known from studies on other molecular crystals (see below), and χ_ν can be semiempirically estimated, then also the ts modes can be used and have been successfully used to estimate ρ.[30,31]

We now turn our attention to the problem of evaluating the e-mv linear coupling constants, the fundamental parameters of the theory. Due to their transferability[5,26] the determination of the *g*'s for a given molecule is essential to the prediction of the properties of the different systems in which the molecule is involved. Although the e-mv coupling constants can be estimated through a priori calculations,[13,32] more reliable values can be obtained from optical data, as first suggested by M. Rice and co-workers.[17] As shown in Equation (11), the e-mv frequency perturbation is the basis for the estimate of the *g*'s. Although Equation (11) has general applicability, in practice the use of *ds* organic semiconductors is preferable. In fact in *m* stack crystals ω_γ (the frequency of the molecule with charge ρ) is not experimentally available and has to be estimated by interpolation (cf. Equation 14); moreover, since quasi-degeneracy of e-mv coupled modes is not infrequent, the determination of the corresponding g's becomes rather uncertain.[5]

The procedure generally adopted in estimating the *g*'s from *ds* CT crystals has been to collect the IR excitation spectrum polarized along the stack axis, and to numerically fit the experimental spectrum with the one calculated on the basis of the conductivity given by the LR theory for a stack of non interacting self dimers.[17,25] For such a system, χ_ν is given by $8\mathcal{M}_{CT}^2/\omega_{CT}e^2a^2$ (*a*: intradimer distance) and is estimated from the spectrum in the CT transition region. However, it has

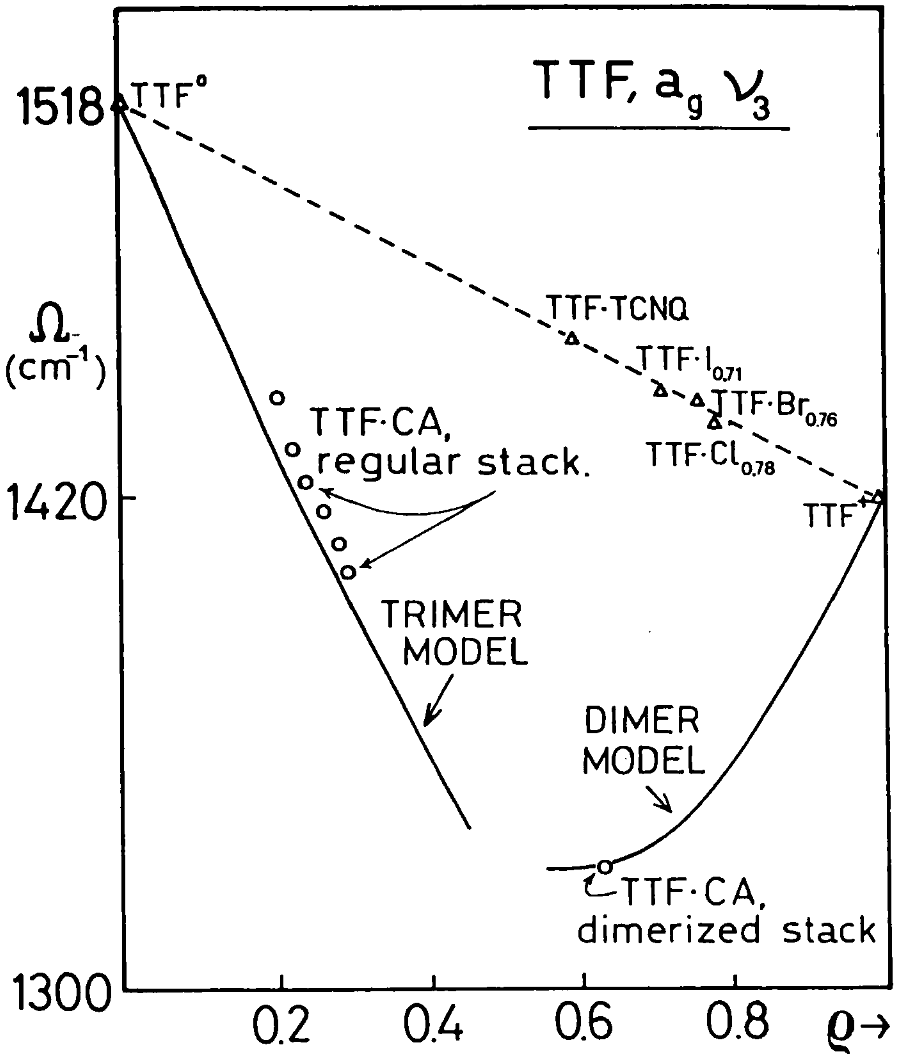


FIGURE 2 Effect of e-mv coupling on the $a_g\nu_3$ frequency of TTF in several organic CT crystals. Dashed line: effect of the quadratic coupling; continuous line: effect of both linear and quadratic couplings. (From Reference 20).

also been shown[26] that a search for the poles of the LR conductivity actually yields a set of linear equations, one for each e-mv coupled mode:

$$\frac{\omega_{CT}^2 - \Omega_\gamma^2}{\omega_{CT}^2} = \sum_\mu \frac{\chi_\nu \omega_\mu g_\mu^2 (\omega_\mu^2 - \Omega_\gamma^2)}{(\omega_\mu^2 - \Omega_\gamma^2)^2 + \Omega_\gamma^2 (\Gamma_\gamma - \gamma_\mu)^2} \tag{16}$$

where γ_μ and Γ_γ indicate the halfwidths of the unperturbed and e-mv perturbed ts modes. Of course analogous equations are also given by the VAM method[5]: in

TABLE II

Linear e-mv coupling constants (meV) for some key molecular structures.

$TCNQ^-$	$KTCNQ^a$	$KTCNQ^b$	$MEM(TCNQ)_2^a$	$MNEB(TCNQ)_2^c$
a_g ν_1	—	—	—	4
ν_2	50	56	44	46
ν_3	53	59	57	58
ν_4	58	64	63	68
ν_5	36	39	32	30
ν_6	8	9	19	7
ν_7	27	29	26	22
ν_8	18	20	16	8
ν_9	39	43	24	19
ν_{10}	—		—	18

TTF^+	$TTFBr^a$	$DBTTF^+$	$DBTTF\ Cu_2Cl_6^d$
a_g ν_2	42	a_g ν_4	19
ν_3	133	ν_5	79
ν_4	—	ν_7	10
ν_5	49	ν_8	16
ν_6	67	ν_{10}	36
ν_7	—	ν_{12}	53

[a] Reference 26. The stack is regarded as a collection of non-interacting self-dimers.

[b] Reference 5. Both intra- and inter-dimer CT interactions are taken into account.

[c] Reference 33. In this work, the nonlinear fitting method has been followed, but keeping the ω_γ's fixed at the values measured from the Raman spectrum.

[d] This work. Only the g's significantly different from zero are reported.

fact, if one neglects the halfwidths and disregards Ω_γ in respect to ω_{CT}, Equation (16), in the form appropriate to the isolated band approximation, reduces to Equation (15). Equation (16) shows that in the determination of the g's the somewhat uncertain nonlinear fitting procedure can be substituted by the solution of a set of linear equations. Moreover, one does not need the detailed shape of the conductivity spectrum, but only the frequencies and halfwidths (Ω_γ and Γ_γ) of the e-mv IR induced bands, which can be obtained also from IR absorption spectra.[26] The other parameters needed to solve Equation (16) in terms of the g's, namely, ω_γ and γ_γ, can also be conveniently measured from the Raman spectra, where the ts modes are not perturbed by e-mv interaction (cf. Figure 1).

The procedure described above has been applied to several TCNQ salts,[26] showing that the e-mv coupling constants are indeed transferable and can be estimated with good accuracy. Table II summarizes the results obtained for $TCNQ^-$ and for two important radical cations, TTF^+ and $DBTTF^+$. In the latter cases however, the measurements have been performed on a single type of radical salt (TTF Br and DBTTF Cu_2Cl_6, respectively), so that their accuracy cannot be definitely assessed.

As already stated in the Introduction, the role of e-mv coupling in organic semiconductors is quite a peculiar one. In fact, although the strength of the single e-mv couplings does not appear to be very large, the high number of e-mv coupled modes makes the collective contribution important in modulating the on-site energies.[34] The energy gain due to the relaxation of the molecular skeleton consequent to the addition (or removal) of one electron, namely, the small polaron binging energy,[32] $\mathcal{E}_{SP} = \sum_\gamma g_\gamma^2/\omega_\gamma$, is a measure of the overall e-mv interaction energy. For example, $\mathcal{E}_{SP}$ of $TCNQ^-$ is about 0.1 eV, of the same order of magnitude as the CT integral (cf. Table I). Therefore, the e-mv coupling must always be taken into account in realistic models of the properties of organic semiconductors. In particular, it has been shown that the e-mv coupling plays an importatnt role in determining the N-I and *r-d* stack instabilities in *m* stack CT crystals.[7] In view of their transferability, the e-mv coupling constants can of course be employed in interpreting the optical data and in modeling the properties of organic conductors and superconductors[1]; however, this important aspect does not concern us here. We shall instead close this Section by mentioning that knowledge of the g's also yields the evaluation of the strength of the intersite Coulomb interaction, $\mathcal{E}_c$, in *rm* stack CT crystals. In fact in such systems χ_ν depends on $\mathcal{E}_c$ as calculated by the valence bond technique.[6] Thus, if ρ is known (from the CT transition or from the non-ts modes), an analysis of the Raman spectra on the basis of Equation (11) yields the value of χ_ν and the corresponding $\mathcal{E}_c$. For TTF-CA at 300 K, such an analysis has given plausible results, in good agreement with the relevant a priori calculations.[35]

V. VIBRATIONAL SPECTROSCOPY AS A STRUCTURAL TOOL

As described in Section III, the consequence of the e-mv interaction on the vibrational spectra of organic semiconductors depends on the stack symmetry, being different for different stack structures. The results summarized in the left part of Figure 1, referring to 1:1 CT crystals, are clearer if we recall that the appearance in the IR spectra of e-mv induced bands, polarized along the stack axis and corresponding to the ts modes of the component molecules, marks the breaking of the on-site inversion center symmetry: the stack is dimerized. In such a case, the frequency coincidence between the IR e-mv induced bands and the corresponding Raman counterparts indicates that the inversion center between molecular sites is also lost: the stack is a mixed one. On the contrary, the lack of coincidence indicates a *ds* stack.[36] These simple rules constitute the basis for the use of vibrational spectroscopy as a powerful and sensitive structural tool.

Before going further, it is worthwhile to analyse in detail how accurate the already described models are in reproducing the experimental e-mv induced IR excitation spectrum. In Figure 3 the experimental[5] (upper part) conductivity spectrum of K TCNQ (*ds* stack), obtained by a Kramers-Krönig analysis of the polarized reflectivity data, is compared with the results of two types of calculations. The middle part of the Figure reports the real part of the conductivity, obtained through the VAM method under the assumption that only one CT electronic transition (intra-dimer) is observed. The lower part of the Figure reports the spectrum calculated by assuming that the observed CT band corresponds to the superposition of two CT transitions (intra- and inter-dimer).[5] It is seen that both calculations reproduce the experimental frequencies well, by using virtually the same set of g's (Table II);

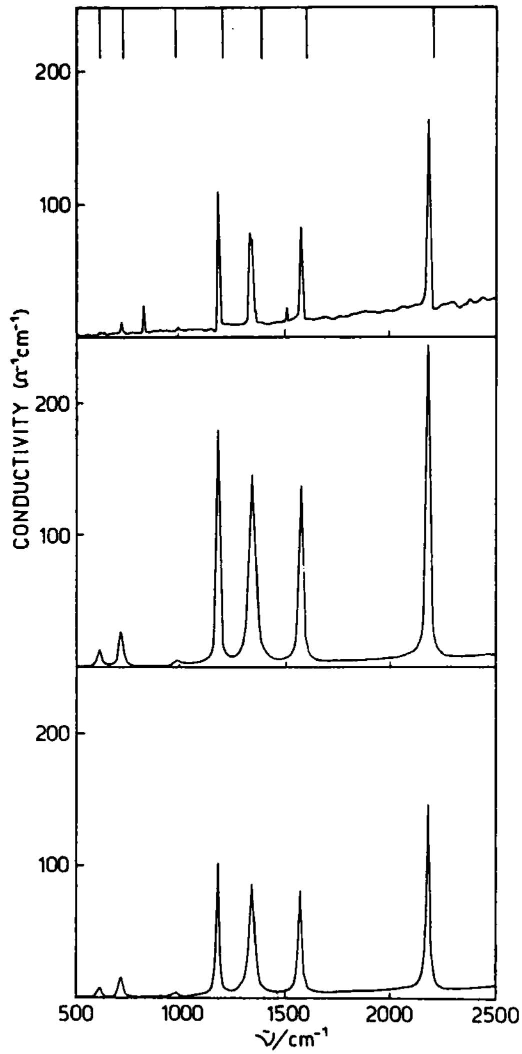


FIGURE 3 Real part of the frequency dependent conductivity of K TCNQ along the stack axis. Upper panel: experimental spectrum. Middle and lower panels: spectra calculated with the VAM model considering one and two electronic CT transitions, respectively. (From Reference 5).

on the other hand the absolute intensities are better reproduced by the spectrum in the lower part of the Figure. The reason for this difference is that the frequencies are connected to the e-mv coupling constants by equations like Equation (15) or (16), where χ_ν is essentially related to the sum of the squared dipole moments of the transitions. In other words, χ_ν depends on the overall intensity of the experimental CT bands(s), and it does not matter whether this corresponds to one or more CT transitions. On the other hand, the intensity of the e-mv induced bands is related to the *difference* between the squared dipole moments of the intra- and inter-dimer CT transitions, thus depending critically on the interpretation of the CT excitation spectrum.

From this and other examples reported in the literature[17,19,25,29,33,37,38] it is clear that the e-mv models described in Section III yield a fairly detailed and reliable interpretation of the experimental spectrum, which is accurately reproduced in the calculations. Of course limitations also come from the experiment itself, in view of the difficulties of obtaining absolute reflectivity data from samples which are often made up by mosaics of small crystals. The point worth underlining in the above example of K TCNQ is that the intensity of the e-mv induced bands is related to the amplitude of the stack distortion (b-CDW), as measured by the so-called asymmetry parameter,[7] $\varphi = (t_i - t_{i+1})/(t_i + t_{i+1})$. Thus, whereas in the calculation it is rarely necessary to reproduce the absolute intensities, as the values of e-mv coupling constants are essentially determined by the frequency values (Section IV), it is important to have a theoretical basis in order to qualitatively relate the intensities of the e-mv induced bands with the b-CDW amplitude. In this way one is able to relate the change of intensity of the e-mv induced IR bands with the change in the amplitude of the b-CDW following a phase transition.

The first application of the above idea, which dates back to more than ten years ago, is in the IR study of the temperature induced *r-d* stack phase transition of K CA.[39] The simple measurement of the peak intensity of an e-mv induced band as a function of *T*, performed by IR absorption spectra of a powdered sample, very neatly displays the occurrence of a *r-d* phase transition, accompanied by a remarkable hysteresis (Figure 4). The same study allowed us to establish that the inclusion of water or acetone molecules in the crystal lattice also yields dimerization

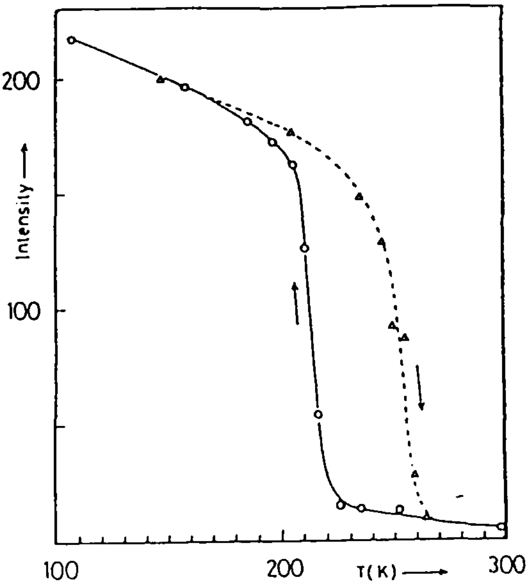


FIGURE 4 Temperature dependence of the peak intensity of the 498 cm^{-1} e-mv IR induced band of K CA. (From Reference 39).

of the stack, as subsequently confirmed by x-ray.[40] Several other examples of *r-d* phase transitions in *s* stack semiconductors have been studied by the above IR method[13,41,42]; the results have generally shown good agreement with parallel studies of other observables, particularly the magnetic susceptibility. In some cases the IR spectra yield results which are more directly interpretable than the magnetic susceptibility data: for instance, in *s*-double stack systems like HMTTF-TCNQF$_4$, two phase transitions occur: one (at 145 K) implies the dimerization of the TCNQF$_4$ stack, and the other (at 95 K) that of the HMTTF stack.[42] The IR measurements directly show the appearance of ts bands of TCNQF$_4$ and of HMTTF at the two temperatures, respectively, whereas the magnetic susceptibility curve has to be deconvoluted to separate the contributions of the two stacks.

The IR technique has also been widely used to study the *r-d* stack phase transitions in *m* stack CT crystals[11,20,29,30,37,38,43]; in this case, however, one also has to control the ionicity of the system, since *m* stack CT crystals may undergo a different type of phase transition, from N to I ground state.[44] Vibrational spectroscopy has widely contributed to the precise characterization of the temperature and pressure induced N—I phase transition of TTF-CA.[20,29-31,45] Figure 5 shows the variation of the degree of ionicity with temperature (right side) and pressure (left side), as measured from the shift of non-ts and ts modes. For the latter, proper account has been taken of the non-linear dependence of the frequency with ρ (Figure 2) due to the e-mv interaction. Figure 5 shows how both temperature and pressure first induce a gradual increase of ρ, followed by a discontinuous jump to a ρ ≃ 0.6 state.

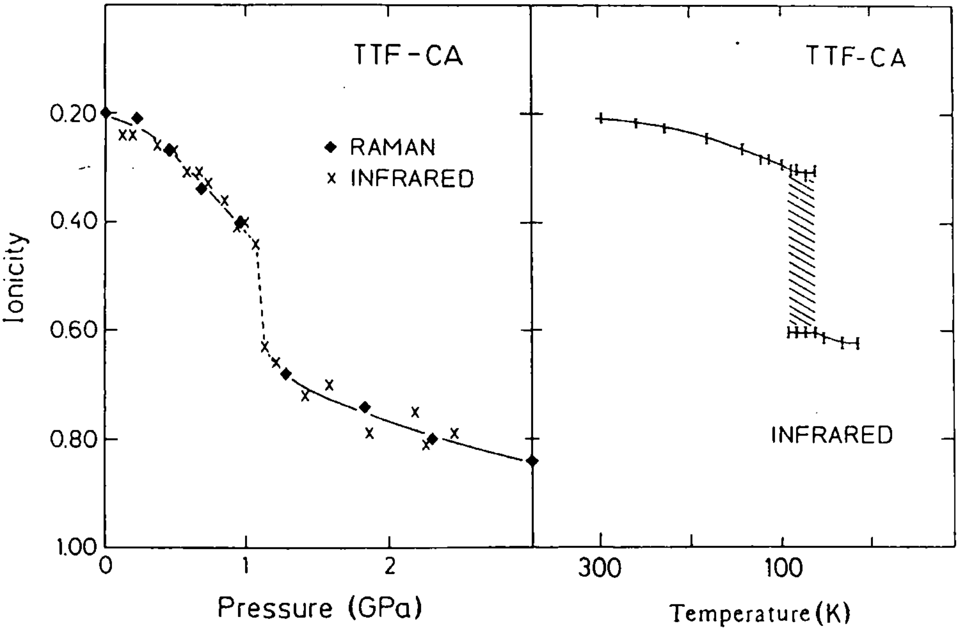


FIGURE 5 Pressure (left side) and temperature (right side) dependence of the ionicity of TTF CA, measured by IR and Raman spectra (From References 31 and 20, respectively).

This jump is accompanied by the appearance of e-mv induced bands in IR, indicating that in both cases the N—I transition is accompanied by stack dimerization.

We shall not go over the details of the differences between temperature and pressure induced N*r*—I*d* phase transitions in TTF-CA, always evidenced through vibrational spectroscopy,[31,45] nor shall we describe the various investigations performed by the Padova group on the different types of ground states and phase transitions occurring in *m* stack CT crystals.[20] Such studies have highlighted the interplay between N—I and *r-d* stack interfaces, and stimulated the subsequent rationalization brought in by the valence bond calculations.[7] We close this Section by underlining that in some cases vibrational spectroscopy yields structural information which is not easy to obtain from x-ray, such as the detection of disorder in the stack structure. In fact static (defects) or dynamic (fluctuations) stack distortions randomly distributed along the chain, not recognized by x-ray, would still give rise to detectable e-mv induced bands in the IR spectra. The occurrence of such bands in the room temperature spectra of TMPD-TCNQ[11] and TMPD-CA[38] has indeed proven that the corresponding x-ray structures, indicating an *r* stack, have to be carefully re-examined.

VI. CONCLUDING REMARKS AND PERSPECTIVES

Through this account of the Padova group research activity we have tried to stress the role of optical spectroscopy, particularly in the spectral region of intramolecular vibrations, in investigating the electronic and structural properties of organic semiconductors. Although we have limited the discussion to four basic stack types, the theoretical framework of e-mv coupling can be considered rather well defined,[5] so that extension to more complex stack structures, such as trimerized *s* stacks like Cs_2TCNQ_3,[19] or DDAADD *m* stacks like TTF-TCNE[46] constitute direct (though involved) applications of the method. The discussion has been limited to organic semiconductors, but the methods we have compactly described here have been applied and, with the appropriate changes, are more extensively applicable to other systems such as organic conductors,[1] transition metal chain compounds[47] or even new, exotic systems like Langmuir-Blodgett films.[48]

Notwithstanding the fairly high degree of sophistication reached by the above described techniques and models, there are a number of open problems that have only recently been approached and which deserve further efforts. For instance, the bond energies are mainly modulated by lattice phonons (Section II), yet the molecular vibrations (for instance the out-of-plane modes) may contribute,[49] though the relevant coupling constants (Equation 7) are generally quite small. In *md* systems molecular modes modulating on-site and bond energies are allowed by symmetry to couple (Figure 1): thus in the case of quasi degeneracy, the modes modulating *t* may interact appreciably with the e-mv coupled ones. The resulting mixing of the modes can give rise to new and somewhat unexpected phenomena, like intensity transfers between the modes. A case in which this type of interaction has been invoked is TMPD-CA,[38] and the corresponding theory has been developed through multidimensional LR methods.[24] The same type of approach allows one to treat electron-phonon coupling in 2D CT systems, and to predict intensity transfers even between differently polarized vibrational modes.[24] The corresponding experimental study and interpretation of the spectra of 2D systems, such as the BEDT-TTF salts, has just been tackled[50] and requires further effort. Another area which needs experimental investigations is that of the coupling between CT electrons and lattice modes. As already mentioned, the e-lph coupling is strongly dependent on structural details and has to be investigated case by case. However the many and varied properties of organic semiconductors which depend on electron-phonon couplings cannot be fully understood before this part of the study has also been carried out.

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