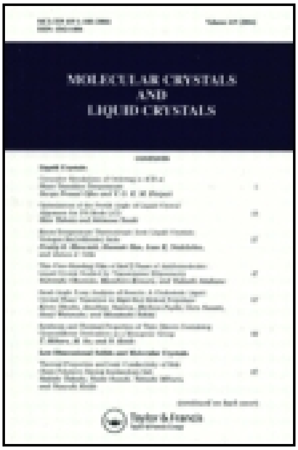

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CS_2 $TCNQ_3$ Revisited: A Detailed Description of its Ground State Through a Reinterpretation of the Optical Spectra

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CS_2TCNQ_3 REVISITED: A DETAILED DESCRIPTION OF ITS GROUND STATE THROUGH A REINTERPRETATION OF THE OPTICAL SPECTRA

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Abstract A substantially complete and definite interpretation of Cs_2TCNQ_3 infrared and Raman spectra (in the region of intramolecular modes) is achieved. The presence of vibronic absorptions in the infrared spectra is quantitatively accounted for in terms of a newly introduced model of electron-molecular vibration (e-mv) interaction, which takes into consideration the coupling with both the intra- and inter-trimer charge transfer transitions. The same model, with the same parameters, is also able to explain the so far unrecognized e-mv perturbation (frequency shift) of the Raman active totally symmetric modes. The re-examination of the Cs_2TCNQ_3 optical spectra thus shows that the electronic charge on the Cs_2TCNQ_3 molecular sites differs appreciably from zero and one, being 0.1_4 and 0.9_3 for centric and non-centric TCNQ molecules, respectively.

INTRODUCTION

In the field of quasi one-dimensional organic conductors the Cs_2TCNQ_3 salt, prototype of 2:3 TCNQ (7,7,8,8-tetracyanoquinodimethane) compounds, is a remarkable example of the rather subtle interplay of the factors which determine the electronic structure and hence the conductivity of these compounds.[1] The formal 2:3 (0.67) electronic charge per molecule (ρ), would in fact suggest a low effective electron-electron repulsion, and correspondingly an high conductivity. However, Cs_2TCNQ_3 is a semiconductor, with a room temperature conductivity [2] ($\sim 10^{-3}\Omega^{-1}$ cm^{-1}) only slightly higher than that of 1:1 salts like KTCNQ. The numerous studies [3-7] dedicated to Cs_2TCNQ_3 have shown that the low conductivity is associated with an uneven distribution of the electronic charge along the TCNQ stack. The latter in fact is made up of repetitive trimeric units, [3] with two charged molecules sandwiching a neutral one. [3,4] The localized nature of the electronic states is confirmed by the presence of two charge transfer (CT) transitions,[5] one between the neutral molecule and the anions (intra-trimer, CT1) and the other between the anions themselves (inter-trimer, CT2). Therefore the electronic charge along the TCNQ stack forms a "pinned charge density wave", probably induced by the cations' Coulomb potential.[1,7]

Although the above sketched picture of the Cs_2TCNQ_3 electronic ground state seems rather well defined, a couple of crucial questions remains open, both related to the interpretation of the vibrational spectra and to the basic molecular parameters derived from them. First of all, despite several other vibrational studies that have appeared[6-8] after the first one, [4] a more precise determination of the TCNQ's ρ values has not been reported. As will be shown in detail in next Section, the problem is that the ρ values inferred from the Raman data are not consistent among themselves or with those coming from the infrared (IR) spectra (although in both cases they appear to depart significantly from one and zero). Secondly, the studies [6,9] performed on the electron-molecular vibration (e-mv) interaction in Cs_2TCNQ_3 give improper values for the e-mv coupling constants.[10]

Aim of the present paper is to overcome the above sketched interpretative problems, and obtain a detailed description of the Cs_2TCNQ_3 electronic ground state. At the same time we shall introduce a new theoretical model, able to properly account for the effects of e-mv interaction on the IR and Raman spectra of segregated, trimerized stack CT crystals.

INFRARED AND RAMAN SPECTRA

Despite the numerous studies on Cs_2TCNQ_3 IR and Raman spectra,[4,6-9] a Table reporting all the observed experimental frequencies and their assignment is still lacking. The only one available concerns the IR data, and is limited by a poor signal to noise ratio in some of the reported spectral regions. Table I therefore fills this gap by reporting the observed IR frequencies of both Cs_2TCNQ_3 and its fully deuterated analogue, $Cs_2(TCNQd_4)_3$, and the Raman ones of Cs_2TCNQ_3, from 2250 to 200 cm^{-1}. All the data refer to powdered samples of the salt, which has been prepared as previously reported.[4,11] Conventional Nujol and perfluorocarbon mulls have been used for the IR spectra, recorded with a Perkin Elmer 580B grating spectrometer. The rotating cell technique[12] has been adopted for the Raman spectra, obtained with a Spex 1403 spectrometer and a Spectra Physics 165 Ar ion laser.

Apart from the better resolution and the detection of additional weak bands, the Cs_2TCNQ_3 IR data in Table I substantially agree with those reported by Cummings *et al.*[6] Instead, we have not detected the strong Raman band at 1452 cm^{-1} reported by Bandrauk *et al.*[7] neither with the 514.5 nm excitation (Table I and Ref. 4) nor with the 457.9 nm one, which should give enhanced intensity.[7] However, we have observed that such a band appears when the laser power is brought beyond a threshold value. Since its frequency coincides with that of a band of neutral TCNQ,[13] we believe that its presence in the reported Cs_2TCNQ_3 Raman spectra[7] is due to contamination by neutral TCNQ, included during the preparation of the salt[14] or produced by a laser thermal decomposition.

Having ascertained the spurious origin of the 1452 cm^{-1} band, the assignment of Cs_2TCNQ_3 Raman spectrum (Table I, column two) follows directly from the comparison with the well known assignments of fully neutral and ionic TCNQ.[11,13] The assignment of the Cs_2TCNQ_3 IR spectrum is instead more difficult due to the presence (in addition to the normally IR active *ungerade* modes) of vibronic IR absorptions. These absorptions are associated with the totally symmetric (a_g)

TABLE I. Raman and Infrared Spectra of Cs_2TCNQ_3, and Infrared Spectrum of $Cs_2(TCNQd_4)_3$

Cs_2TCNQ_3 Raman [a]		Cs_2TCNQ_3, Infrared		$Cs_2(TCNQd_4)_3$, Infrared	
Frequency [b]	Assignment [c]	Frequency [b]	Assignment [c]	Frequency [b]	Assignment [c]
2224 w	a_g ν_2° (2229)	2225 mw	b_{1u} ν_{19}° (2228)	2226 mw	b_{1u} ν_{19}° (2229)
2213 w		2211 mw	b_{2u} ν_{33}° (2228)	2212 mw	b_{2u} ν_{33}° (2229)
2194 m	a_g ν_2^{-} (2206)	2189 s	e-mv	2189 s	e-mv
		2184 sh		2181 s	b_{1u} ν_{19}^{-} (2179)
		2179 s	b_{1u} ν_{19}^{-} (2281)	2167 s	b_{2u} ν_{33}^{-} (2162)
		2160 s	b_{2u} ν_{33}^{-} (2153)	1562 w	
1605 m	a_g ν_3^{-} (1615)	1580 m	e-mv	1553 mw	
1591 s	a_g ν_3° (1602)	1533 m	b_{1u} ν_{20}° (1545)	1539 m	e-mv
		1504 s	b_{1u} ν_{20}^{-} (1504)	1518 m	b_{1u} ν_{20}° (1533)
		1480 w		1504 mw	b_{2u} $\nu_{34}^{\circ -}$
1436 s	a_g ν_4° (1454)	1368 m	b_{1u} ν_{21}^{-}?(1361)	1462 s	b_{1u} ν_{20}^{-} (1461)
1386 s	a_g ν_4^{-} (1391)	1358 s	e-mv	1439 w	
1332 w	b_{3g} $\nu_{44}^{\circ -}$?	1351 sh	b_{2u} ν_{35}°?(1354)	1346 s	e-mv
		1327 w		1315 mw	b_{2u} ν_{35}^{-} (1320)
		1211 m	b_{2u} ν_{36}^{-} (1211)	1306 w	b_{2u} ν_{35}° (1316)
		1205 sh	b_{2u} ν_{36}° (1209)	1233 w	b_{1u} ν_{21}° (1246)
1189 s	a_g ν_5^{-} (1196)	1184 s	e-mv	1218 w	b_{1u} ν_{21}^{-} (1222)
1178 sh	b_{3g} ν_{45}^{-} (1179)	1177 sh		1178 mw	b_{2u} ν_{36}^{-} (1181)
		1132 w	b_{2u} ν_{37}^{-}?(1125)	971 mw,br	b_{1u} $\nu_{22}^{\circ -}$, e-mv ?
		1113 w	b_{1u} ν_{22}^{-} (1008)	864 m	e-mv
		1002 w	b_{1u} ν_{22}^{-} (998)	848 m	b_{2u} ν_{37}° (855)
		984 mw	b_{1u} ν_{23}^{-} (987)	845 m	b_{2u} ν_{37}^{-} (840)
967 w	a_g ν_6^{-} (978)	972 w	e-mv	822 w	b_{1u} ν_{23}^{-} (826)
955 w	a_g ν_6° (955)	964 w	b_{1u} ν_{23}° (962)	802 m	b_{1u} ν_{23}° (801)
		955 mw		777 w	
		837 m	b_{3u} ν_{50}^{-} (859)	741 m	b_{3u} ν_{50}° (756)
		824 m	b_{3u} ν_{50}° (836)	724 m	b_{3u} ν_{50}^{-} (732)
		807 w		696 mw	e-mv
723 w	a_g ν_7^{-} (725)	724 mw	e-mv	652 w	
707 w	a_g ν_7° (711)	717 mw		617 w	b_{1u} $\nu_{24}^{\circ -}$
		617 w	b_{1u} $\nu_{24}^{\circ -}$	600 w	e-mv
620 w	a_g ν_8^{-} (613)	608 w	e-mv	585 w	
611 w	a_g ν_8° (602)	569 mw	b_{3u} ν_{51}^{-}? (585)	562 mw	b_{3u} ν_{51}^{-} (565)
587 w	b_{2g} ν_{29}° (593)	545 w	b_{1u} $\nu_{25}^{\circ -}$	530 w	b_{1u} $\nu_{25}^{\circ -}$
570 w	b_{2g} ν_{29}^{-} (570)	510 w	b_{2u} ν_{38}^{-} (512)	507 w	b_{2u} ν_{38}^{-} (512)
		500 w	b_{2u} ν_{38}° (498)	497 w	b_{2u} ν_{38}° (496)
		484 m	b_{3u} ν_{52}^{-} (483)	425 m	b_{3u} ν_{52}^{-} (423)
		469 mw	b_{3u} ν_{52}° (475)	408 mw	b_{3u} ν_{52}° (418)
352 w		344 w		348 w	
329 m	a_g $\nu_9^{\circ -}$	326 mv	e-mv	326 mw	e-mv
306 w		224 mv	b_{3u} $\nu_{53}^{\circ -}$	220 mw	b_{3u} $\nu_{53}^{\circ -}$

[a] *Exciting line 514.5 nm.* [b] *Frequencies in wavenumbers. Qualitative relative intensities indicated by: s, strong; m, medium; mw, medium weak; w, weak; sh, shoulder; br, broad.* [c] *Classification and numbering of the normal modes as in Ref. 11 ; e-mv marks the e-mv induced infrared absorptions (corresponding to a_g modes). The "°" and "−" superscripts indicate the assignment to quasi-neutral and to quasi-ionic TCNQ units, respectively; the corresponding frequencies of fully neutral and ionic molecules (Ref. 11) are reported in parenthesis.*

modes of the isolated molecular species and were indeed misassigned in early work.[4] They have subsequently been well identified from the vibrational studies of dimerized stack TCNQ salts, [11,15] their origin being recognized as due to the interaction of the molecular vibrations with the CT electron. The previously reported [6] polarized IR reflectance spectra of Cs_2TCNQ_3 , together with correlative criteria, lead to a clear disentangling of these vibronic absorptions (marked by "e-mv" in columns four and six of Table I) from the other ones. For the assignment of the normally IR active bands one can also exploit the information derived from the frequency shifts of the deuterated compound. On this basis and from the comparison with the spectra of other TCNQ CT salts,[16] we modify two of the assignments proposed in Ref. 6, precisely those of the 1504 and 2160 cm^{-1} bands, which we attribute to the b_{1u} ν_{20} and b_{2u} ν_{33} modes of the ionized molecule instead that to the b_{2u} ν_{34} and b_{1u} ν_{19} respectively (in both cases the indications coming from the polarized spectra [6] are dubious, due to the overlapping by nearby bands). The overall assignment of the Cs_2TCNQ_3 and $Cs_2(TCNQd_4)_3$ IR spectra is reported in columns four and six of Table I.

Having achieved a reliable and substantially complete interpretation of the Cs_2TCNQ_3 vibrational spectra, we now turn to the problem of the precise determination of the electronic charge residing on the molecular sites (ρ). Previous studies [4,6] have pointed out that the Cs_2TCNQ_3 spectra are essentially a superposition of bands belonging to $TCNQ^0$ and $TCNQ^-$. For simplicity, we have maintained this scheme in the assigned columns of Table I. A careful comparison with the frequencies of fully neutral and ionic TCNQ (as results from Table I) shows however that the Cs_2TCNQ_3 ρ values are appreciably different from zero (neutral) and one (ionic). On the other hand, the well known and tested procedure for the determination of ρ by vibrational spectroscopy [17,18] presents a problem. In fact, if we use the *ungerade* IR diagnostic frequencies, i.e., the b_{1u} ν_{19}, ν_{20} and ν_{23} and the b_{2u} ν_{33} of both light and deuterated compounds, and perform the usual weighted average,[18] we end up with ρ values of 0.1_4 and 0.9_3 ($\pm$0.1) for the quasi-neutral and the quasi-ionic TCNQ, respectively. The Raman a_g frequencies give instead ρ values not very well consistent with the above ones or among themselves: the a_g ν_2 gives 0.5 and 1.4, the ν_4 0.3 and 1.1, the ν_6 0.2 and 0.6, for the quasi-neutral and quasi-ionic TCNQ, respectively.This fact is somewhat surprising, as the a_g Raman modes, and in particular the ν_4 one, are known to give rather accurate ρ values, [17] at least for segregated stack compounds.[18] Clearly, some *specific* perturbation has to be present to affect the Raman data. As we shall see in the next Section, such perturbation is another, so far unrecognized manifestation of the e-mv interaction in trimerized segregated stack compounds like Cs_2TCNQ_3 .

As we have mentioned above,the most dramatic and well known manifestation of e-mv interaction is the appearance of strong IR absorptions, polarized along the stack axis (like the CT transitions) and corresponding to the totally symmetric modes of the isolated molecule. A quantitative model of the effect of e-mv interaction on the IR spectra, able to account for the presence of such bands in the spectra of *dimerized* segregated stack systems had been proposed by M.J. Rice some years ago.[19] In terms of such a model one is able to extract from optical spectra key microscopic parameters, like U (the effective Hubbard on site repulsion energy), t (the CT integral) and g_α, the e-mv linear coupling constants defined by:

$$g_\alpha = \frac{1}{(2\hbar\,\omega_\alpha)^{\frac{1}{2}}} \left(\frac{\partial \varepsilon_{MO}}{\partial Q_\alpha}\right)_0 \qquad (1)$$

where ε_{MO} is the energy of the CT molecular orbital, and Q_α the normal coordinate corresponding to the vibrational mode of frequency ω_α. Unlike U and t, the g's are molecular parameters, and as such they should be transferable among crystals of different kind. [10]

The strong bands polarized along the stack axis detected [6] in the IR spectra of Cs_2TCNQ_3 have clearly the same vibronic origin as those encountered in dimerized stack CT crystals.[11,19] Cs_2TCNQ_3 , however, is not a dimerized stack system, the TCNQ chain being made up by repetitive *trimeric* units, [3] with two CT transitions, around 3900 cm^{-1} (CT1, intra-trimer) and around 10000 cm^{-1} (CT2, inter-trimer). [5,6] Despite this

Cummings *et al.*[6] have applied to the Cs_2TCNQ_3 e-mv induced spectrum Rice's dimer model.[19] However, only the ion-ion, inter-trimer CT2 transition is thus taken into account. Subsequently Yartsev [9] has extended the Rice's model to isolated trimeric units. In such a way then one considers the CT1, intra-trimer transition, but disregards the CT2. Table II shows that the g_α values obtained by these two approaches differ considerably among themselves, and appear also different from the values previuosly determined from KTCNQ, contradicting the criterion of transferability.[10] Clearly, the assumption that in Cs_2TCNQ_3 only one CT transition should interact with the molecular vibrations appears untenable, both the CT's being coupled to the TCNQ a_g modes. In the next Section we introduce a new model of e-mv interaction in trimerized segregated stack systems, able to take into account (at least in an approximate, semiempirical way) both the CT transitions, and to explain the e-mv perturbation of the Raman spectra.

TABLE II. Cs_2TCNQ_3 e-mv coupling parameters

a_g	$g_\alpha(\text{meV})^a$	$g_\alpha(\text{meV})^b$	$g_\alpha(\text{meV})^c$	$\Gamma_\alpha\ (\text{cm}^{-1})^c$
ν_2	64	17	50	18
ν_3	89	17	53	12
ν_4	106	25	58	12
ν_5	71	19	36	5
ν_6	--	--	8	15
ν_7	--	--	27	15
ν_8	10	11	18	15
ν_9	30	--	39	15

[a] Ref. 6. [b] Ref. 9. [c] This work; e-mv coupling constants relevant to KTCNQ (Ref. 10).

e-mv INTERACTION IN TRIMERIZED SEGREGATED STACKS

The problem of e-mv interaction in quasi one-dimensional organic semiconductors is conveniently tackled by perturbation methods, starting of course from the solution of the purely vibrational and electronic parts of the Hamiltonian.[20] Analytical, exact solutions of the latter cannot however be found for an infinite chain of molecules, since one should start from a very large (actually infinite) number of basis wavefunctions. To reduce the basis set, one can choose between two basically different approximations. In the first one, the chain is broken into smaller units, disregarding the CT integrals between the units themselves. As we have seen, this approach does not lead to satisfactory results when applied to Cs_2TCNQ_3.[6,9] We shall therefore adopt the second kind of approximation, which consists in disregarding the highest energy wavefunctions, taking, however, into account both intra-and inter-trimer CT integrals.[20]

We choose the simplest possible starting basis set, made up by the following five electronic wavefunctions (we do not consider explicitly the spin degrees of freedom):

$$\begin{aligned}
\Phi^{o} &= \prod_{i} | A^{-}_{\ell,i} \; A^{o}_{c,i} \; A^{-}_{r,i} \rangle = \prod_{i} \psi_i \\
\Phi^{1}_{i r} &= | A^{o}_{\ell,i} \; A^{-}_{c,i} \; A^{-}_{r,i} \rangle \prod_{j \neq i} \psi_j \\
\Phi^{1}_{i \ell} &= | A^{-}_{\ell,i} \; A^{-}_{c,i} \; A^{o}_{r,i} \rangle \prod_{j \neq i} \psi_j \qquad (2) \\
\Phi^{2}_{i r} &= | A^{-}_{\ell,i} \; A^{o}_{c,i} \; A^{o}_{r,i} A^{=}_{\ell,i+1} A^{o}_{c,i+1} \; A^{-}_{r,i+1} \rangle \prod_{j \neq i,i+1} \psi_j \\
\Phi^{2}_{i \ell} &= | A^{-}_{\ell,i} \; A^{o}_{c,i} \; A^{=}_{r,i} A^{o}_{\ell,i+1} A^{o}_{c,i+1} \; A^{-}_{r,i+1} \rangle \prod_{j \neq i,i+1} \psi_j
\end{aligned}$$

where i counts the N trimeric units in the chain, and A stands for the site molecular orbital (not occupied, singly and doubly occupied: A^0, A^- and $A^=$, respectively); the ℓ, c and r indices refer of course to the left, central and right site within a trimer. Thus the lowest energy wavefunction is a product of trimer wavefunctions, each trimer being made up of fully ionic molecules sandwiching a fully neutral one. Then we have 2N intra-trimer excitonic wavefunctions, corresponding to the left and right transfer of one electron within the trimer; finally, there are the corresponding excitonic wavefunctions for the inter-trimer electron transfer.

The left and right excitonic wavefunctions are degenerate, and combine to give $\Phi_i^{1\pm}=2^{-\frac{1}{2}}(\Phi_{ir}^{1} \pm \Phi_{i\ell}^{1})$ and $\Phi_i^{2\pm}=2^{-\frac{1}{2}}(\Phi_{ir}^{2} \pm \Phi_{i\ell}^{2})$. In the k=0 subspace, the only one we shall consider in the following, they become:

$$\Phi^{1+}=N^{-\frac{1}{2}}\sum_i \Phi_i^{1+} \quad ; \quad \Phi^{1-}=N^{-\frac{1}{2}}\sum_i \Phi_i^{1-}$$
$$\Phi^{2+}=N^{-\frac{1}{2}}\sum_i \Phi_i^{2+} \quad ; \quad \Phi^{2-}=N^{-\frac{1}{2}}\sum_i \Phi_i^{2-} \qquad (3)$$

The electronic Hamiltonian mixes Φ^0 only with the Φ^{1+} and Φ^{2+} wavefunctions, yielding:

$$\begin{aligned}
\Psi_1 &= c_0\Phi^0 + c_1\Phi^{1+} + c_2\Phi^{2+} \\
\Psi_2 &= a_0\Phi^0 + a_1\Phi^{1+} \\
\Psi_3 &= b_0\Phi^0 + b_1\Phi^{2+} \qquad (4) \\
\Psi_4 &= \Phi^{1-} \\
\Psi_5 &= \Phi^{2-}
\end{aligned}$$

The two dipole allowed CT transitions are $\Psi_4 \leftarrow \Psi_1$ and $\Psi_5 \leftarrow \Psi_1$ (from the symmetric ground state to the antisymmetric states), at frequency ω_{CT1} and ω_{CT2}, and with squared dipole moment per unit cell given by:

$$\mu_{CT1}^2 = c_1^2\, e^2 a_1^2/N \quad ; \quad \mu_{CT2}^2 = c_2^2\, e^2 a_2^2/N \qquad (5)$$

where a_1 and a_2 are the intra- and inter-trimer distances, respectively, measured along the stack axis, and e is the electronic charge. We notice at this point that the restriction to only five basis wavefunctions leads to an inconsistency: if the CT transitions have finite intensities, the weights (c_1^2, c_2^2) of the excited wavefunctions in the ground state tend to infinity for N tending to infinity. In the following the problem will be avoided by a semiempirical approach, in which the values of μ^2_{CT1} and μ^2_{CT2} are evaluated directly from experimental spectral intensities.

For what concerns the purely vibrational part of the problem we have only to remark that the molecular coordinates, $Q_{c_{i},\alpha}$ for the central molecule and $\tilde{Q}_{ri,\alpha}$, $\tilde{Q}_{\ell i,\alpha}$ for the external ones, are combined in the k=0 subspace to give:

$$S_\alpha = N^{-\frac{1}{2}} \sum_i S_{\alpha,i} ; \quad A_\alpha = N^{-\frac{1}{2}} \sum_i A_{\alpha,i} \quad ; \quad \mathcal{Q}_\alpha = N^{-\frac{1}{2}} \sum_i Q_{ci,\alpha} \qquad (6)$$

where:

$$S_{\alpha,i} = 2^{-\frac{1}{2}} (\tilde{Q}_{\ell i,\alpha} + \tilde{Q}_{ri,\alpha}) \quad ; \quad A_{\alpha,i} = 2^{-\frac{1}{2}} (\tilde{Q}_{\ell i,\alpha} - \tilde{Q}_{ri,\alpha}) \qquad (7)$$

If the Q's refer to the totally symmetric modes (the only ones which can have the g's different from zero [19]) of a centrosymmetric molecule like TCNQ, it is easy to realize that S_α and $\mathcal{Q}_\alpha$ are active only in the Raman, whereas A_α is active only in the IR.

We turn now our attention to the electron-molecular vibration interaction Hamiltonian, which reads ($\hbar$ = 1):[19, 20]

$$H_{ev} = \sum_{i,\alpha} 2^{\frac{1}{2}} (\tilde{\omega}_\alpha^{\frac{1}{2}} \tilde{g}_\alpha n_{i\ell} Q_{\ell i,\alpha} + \omega_\alpha^{\frac{1}{2}} g_\alpha n_{ic} Q_{ci,\alpha} + \tilde{\omega}_\alpha^{\frac{1}{2}} \tilde{g}_\alpha n_{ir} Q_{ri,\alpha})$$

where n_i is the electron occupation number operator. In terms of the symmetry adapted coordinates of Eq.(7) H_{ev} can be rewritten as:

$$H_{ev} = \sum_{i,\alpha} \tilde{g}_\alpha \tilde{\omega}_\alpha^{\frac{1}{2}} \{(n_{i\ell} + n_{ir}) S_\alpha + (n_{i\ell} - n_{ir}) A_\alpha\} + $$

$$+ \sum_{i,\alpha} (2\omega_\alpha)^{\frac{1}{2}} g_\alpha n_{ic} \mathcal{Q}_\alpha \qquad (9)$$

As shown in detail elsewhere, [20] the introduction of quadratic coupling terms in Eqs.(8) and (9) simply leads to a renormalization of the vibrational frequencies (and of the e-mv coupling constants), from those of the initially chosen reference nuclear configuration to those of the new nuclear equilibrium position for the molecule in the crystal. Thus all the interesting physics can be deduced from the linear e-mv Hamiltonian, provided that the frequency variation is introduced semiempirically. Henceforth therefore ω_α and $\tilde{\omega}_\alpha$ (g_α and $\tilde{g}_\alpha$) stand for the frequency (e-mv coupling constant) of the central and external molecules, with the electronic charge they have in the crystal.

At this point, the usual procedure[19, 21] would be to apply the linear response theory to calculate the response of the system, perturbed by H_{ev}, to the radiation field. Here we shall use instead an equivalent, alternative approach, which has the advantage of leading to equations of simple structure, thus allowing a clear insight into the physics of the problem. The details of the method, which we have called Vibronic Adiabatic Mulliken (VAM) theory, are reported elsewhere.[20] In the first step of the VAM approach, the perturbative H_{ev} is introduced *via* an Herzberg-Teller expansion, carried out to the second order, on the zero-order electronic wavefunctions of Eq.(4). The ground-state energy thus is written as:

$$E_{GS} = E_1 + < \Psi_1 \mid H_{ev} \mid \Psi_1 > - \frac{\sum_{m=2}^{5} \mid < \Psi_1 \mid H_{ev} \mid \Psi_m > \mid^2}{E_m - E_1} \qquad (10)$$

where E_1 is the zero-order energy associated with Ψ_1. The second derivative of E_{GS} with respect to the normal coordinates gives a sort of "force constant" matrix, whose diagonalization yields the e-mv perturbed frequencies. We focus first our attention on the A_α, IR active modes. The elements of the force constant matrix are:

$$F(A_\alpha, A_\alpha) = \tilde{\omega}_\alpha^2 - 2\tilde{g}_\alpha^2 \, \tilde{\omega}_\alpha \left(\frac{\mu^2_{CT1}}{e^2 a_1^2 \, \omega_{CT1}} + \frac{4\mu^2_{CT2}}{e^2 a_2^2 \, \omega_{CT2}} \right) \qquad (11a)$$

$$F(A_\alpha, A_\beta) = -2\tilde{g}_\alpha \tilde{g}_\beta \, (\tilde{\omega}_\alpha \, \tilde{\omega}_\beta)^{\frac{1}{2}} \left(\frac{\mu^2_{CT1}}{e^2 a_1^2 \, \omega_{CT1}} + \frac{4\mu^2_{CT2}}{e^2 a_2^2 \, \omega_{CT2}} \right) \qquad (11b)$$

If the off-diagonal terms are small in comparison with a diagonal one, that is, if one vibrational mode is well separated in frequency from the other ones (isolated band approximation), its e-mv perturbed frequency, Ω_α^2 ,is of course given directly by Eq.(11a). Its IR intensity can be obtained from the square of the first derivative of the ground state dipole moment, $\mu_{GS} = \langle \Psi_{GS} | \mu | \Psi_{GS} \rangle$, where μ is the dipole moment operator per unit cell and Ψ_{GS} the ground state wavefunction corresponding to the above written energy E_{GS} . One obtains:

$$\mu_\alpha^2 = \frac{1}{2\tilde{\omega}_\alpha^2} \left(\frac{\partial \mu_{GS}}{\partial A_\alpha} \right)_0^2 = 2\tilde{g}_\alpha^2 \left(\frac{2\mu_{CT2}^2}{ea_2\, \omega_{CT2}} - \frac{\mu_{CT1}^2}{ea_1\, \omega_{CT1}} \right)^2 \tag{12}$$

We see that the frequency shifts (with respect to the unperturbed frequencies $\tilde{\omega}_\alpha$) and the intensities of the e-mv induced IR bands are related to the squares of the transition dipole moments of *both* the CT transitions. Notice however that these quantities add up in determining the frequency shifts, but subtract in the expression of the intensities. Thus in trimerized stack systems the vibronic IR absorptions are more shifted, but less intense than that expected by considering the effect of only one CT transition, as done previously for the case of Cs_2TCNQ_3 .[6,9]

In order to calculate the complete IR excitation spectrum from Eqs.(11) and (12),one has to recognize that the A_α modes borrow intensity from the CT transitions: they do not couple to the external electric field (F) directly, but through the time dependent electronic dipole moment(s), μ_{CT} (t) generated by it:

$$\mu_{CT}(t) = \int_{-\infty}^{t} \phi_{CT}(t-t')\, F(t')dt' \tag{13}$$

where ϕ_{CT} (t-t') is the purely electronic response function. μ_{CT} acts as an external field on the molecular vibrations giving rise to a second term in the total dipole moment:

$$\mu(t) = \mu_{CT}(t) + \int_{-\infty}^{t} \phi_v(t-t')\, \mu_{CT}(t')dt' \tag{14}$$

where ϕ_ν is the vibrational response function. The Fourier transform of Eq.(14) gives the total complex susceptibility, $\chi(\omega)$, as $\chi(\omega) = \chi_{CT}(\omega)[1 + \chi_\nu(\omega)]$, where $\chi_{CT}(\omega)$ is the CT electronic susceptibility:

$$\chi_{CT}(\omega) = \chi_{CT1}(\omega) + \chi_{CT2}(\omega) =$$

$$= \frac{2\omega_{CT1}\ \mu^2_{CT1}}{\omega^2_{CT1} - \omega^2 - i\omega\gamma_{CT1}} + \frac{2\omega_{CT2}\ \mu^2_{CT2}}{\omega^2_{CT2} - \omega^2 - i\omega\gamma_{CT2}} \qquad (15)$$

and $\chi_\nu(\omega)$ is the vibrational part:

$$\chi_\nu(\omega) = \sum_\alpha \frac{2\,\Omega_\alpha\ M_\alpha}{\Omega^2_\alpha - \omega - i\omega\Gamma_\alpha} \qquad (16)$$

where the factor M_α, which determines the intensity of the vibronic bands, is related to μ^2_α of Eq.(12) by: $M_\alpha = \mu^2_\alpha / \chi_{CT}(0)$.[20] From the above equations one then derives the following expression for the frequency dependent conductivity of the system, in SI units:

$$\sigma(\omega) = -6.09\cdot 10^{-5}\, i\omega e^{-2} N_t \{\chi_{CT1}(\omega)\ \Big(1 + \sum_\alpha \frac{\Lambda_{1\alpha}\,\Omega^2_\alpha}{\Omega^2_\alpha - \omega^2 - i\omega\Gamma_\alpha}\Big) + \chi_{CT2}(\omega)\ \Big(1 - \sum_\alpha \frac{\Lambda_{2\alpha}\,\Omega^2_\alpha}{\Omega^2_\alpha - \omega^2 - i\omega\Gamma_\alpha}\Big)\} \qquad (17)$$

where N_t is the number of trimers per unit volume, and:

$$\Lambda_{1\alpha} = \frac{2}{ea_1}\ \{\frac{2\mu^2_{CT2}}{ea_2\ \omega_{CT2}} - \frac{\mu^2_{CT1}}{ea_1\ \omega_{CT1}}\}\ \frac{G^2_\alpha}{\Omega_\alpha} \qquad (18a)$$

$$\Lambda_{2\alpha} = \frac{4}{ea_2}\ \{\frac{2\mu^2_{CT2}}{ea_2\ \omega_{CT2}} - \frac{\mu^2_{CT1}}{ea_1\ \omega_{CT1}}\}\ \frac{G^2_\alpha}{\Omega_\alpha} \qquad (18b)$$

in which $G_\alpha = \Sigma_\beta L_{\beta\alpha}\,\tilde{g}_\beta$ is the linear combination of the g's. The combination accounts for the mixing of the A_α modes, $L_{\beta\alpha}$ being the elements of the matrix which diagonalizes the force constant matrix of Eq.(11).

Eqs.(11) through (18) give the solution for the IR e-mv induced spectrum (A_α modes). We now turn the attention to the Raman active modes, S_α and Q_α. It is well known that the Raman spectra of regular or dimerized segregated stack CT crystals are *not* perturbed by e-mv interaction [17, 19, 21]. It is now easy to see that the same is *not* true for trimerized segregated stack systems. In the isolated band approximation the frequency of one S_α mode is in fact given by:

$$\Omega^2_\alpha = F\,(S_\alpha, S_\alpha) = \tilde{\omega}^2_\alpha - \frac{2\, c_1^2\, a_1^2}{N\, \omega_E}\, \tilde{\omega}_\alpha\, \tilde{g}^2_\alpha \tag{19}$$

where ω_E is the frequency difference between the ground state and the Ψ_2 (symmetric) CT state. An analogous expression is obtained for the Q_α modes. Thus, the Raman frequency of a totally symmetric mode will be found at a frequency different (lower if the band is isolated) from what could be expected on the basis of the degree of ionicity determined from the non-totally symmetric modes which are not perturbed by e-mv interaction.

The problem with Eq.(19) is that some of the quantities appearing in it cannot be evaluated. In fact, as mentioned before, for N tending to infinity the coefficient c_1 and therefore also a_0 tend to infinity (and a_1 in Eq.(4) tends to zero). Whereas the obstacle can be circumvented for c_1^2/N on the basis of Eq.(5), this is not possible for the a_1^2 term. Moreover ω_E is not easily obtained, as the transition $\Psi_2 \leftarrow \Psi_1$ is not allowed in simple one-photon spectroscopies. Therefore, if one wishes to evaluate quantitatively the effect of e-mv interaction on the Raman spectra, one is forced to introduce further approximations into the model. The most logical one is to cut the chain and consider an isolated trimer. This approximation is acceptable for Raman (whereas it is not for IR) since in any case, as shown by Eq.(19), only the intra-trimer CT state Ψ_2 interacts directly with S_α or Q_α modes. For an isolated trimer both c_0 and c_1 coefficients are finite (N=1), and, due to the exclusion of the Φ^{2+} state, $a_1^2 \simeq c_0^2 = (1-c_1^2)$. Moreover in such conditions ω_E can be expressed in term of ω_{CT1} as: $\omega_E = \omega_{CT1}/(1-c_1^2)$. Within the limits of the trimer approximation we then obtain the following expressions for the force constant matrix of the Raman active $\mathcal{S}_\alpha$ and $\mathcal{Q}_\alpha$ modes:

$$\begin{aligned} F\,(\mathcal{S}_\alpha,\mathcal{S}_\alpha) &= \tilde{\omega}_\alpha^2 - 2\tilde{\omega}_\alpha\,\tilde{g}_\alpha^2\,c_1^2(1-c_1^2)^2\omega_{CT1}^{-1} \\ F\,(\mathcal{Q}_\alpha,\mathcal{Q}_\alpha) &= \omega_\alpha^2 - 4\omega_\alpha\,g_\alpha^2\,c_1^2(1-c_1^2)^2\omega_{CT1}^{-1} \qquad (20) \\ F\,(\mathcal{S}_\alpha,\mathcal{Q}_\beta) &= 2(2\tilde{\omega}_\alpha\omega_\beta)^{\frac{1}{2}}\,\tilde{g}_\alpha g_\beta\,c_1^2(1-c_1^2)^2\omega_{CT1}^{-1} \end{aligned}$$

and now the electronic parameters can be evaluated from the intensity (Eq.(5)) and frequency of the CT1, intra-trimer transition.

VAM e-mv MODEL APPLIED TO Cs_2TCNQ_3 IR AND RAMAN SPECTRA

According to the model of e-mv interaction presented in the preceding Section, the IR spectra of trimerized stack semiconductors should be characterized by strong vibronic absorptions, polarized along the stack axis, coupled to both the intra-and inter-trimer CT transitions, and corresponding to the totally symmetric modes of the *external* trimer's molecules. The totally symmetric modes of both central and external molecules are instead seen in the Raman spectra; their frequencies are however perturbed (generally lowered) by e-mv interaction, which in this case involves only the intra-trimer CT state. The perturbing effects being different, there is of course no frequency coincidence between the Raman and the e-mv induced IR frequencies of the external trimer molecules.

The above predictions are all fulfilled by the Cs_2TCNQ_3 spectra. A quantitative test of the model can be performed by substituting the appropriate values of the parameters into the equations, and by calculating on one hand the real part of the conductivity (Eq.(17)), and on the other the Raman frequencies (Eq.(20)). We have proceeded as follows. First, the electronic parameters have been extracted from Fig.6 of Ref.6, performing an appropriate integration over the band area. The results

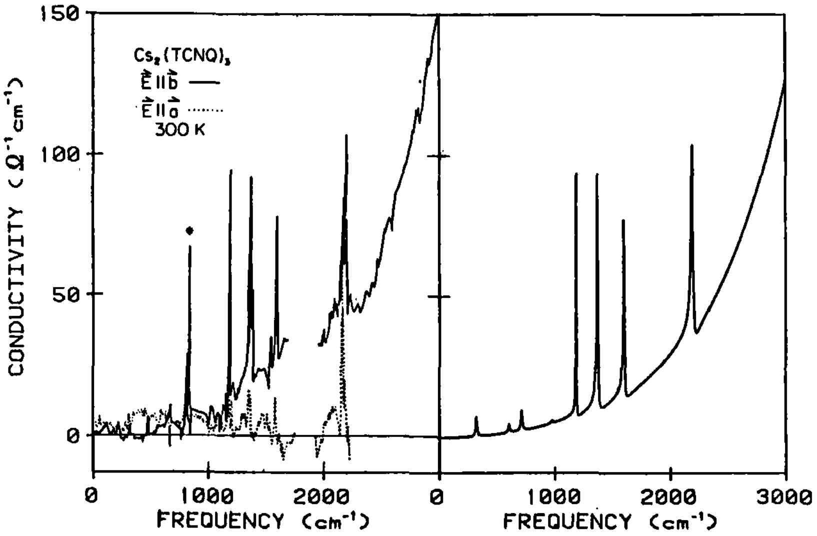

FIGURE 1. Cs_2TCNQ_3 IR conductivity spectra. Left: experimental spectrum (Ref.6); in the polarization parallel to the b stack axis (full line) the asterisk distinguishes the two b_{3u} bands from the e-mv induced ones. Right: calculated vibronic spectrum.

TABLE III. Calculated and observed a_g Raman frequencies (cm^{-1}) of Cs_2TCNQ_3

	$TCNQ^{-0.14}$			$TCNQ^{-0.93}$		
	ω_α	Ω_α^{CAL}	Ω_α^{OBS}	ω_α	Ω_α^{CAL}	Ω_α^{OBS}
a_g ν_2	2226	2219	2219	2208	2198	2194
ν_3	1604	1588	1591	1614	1612	1605
ν_4	1445	1433	1436	1395	1384	1386
ν_5	1205	1201	-	1197	1190	1189
ν_6	953	952	955	976	976	967
ν_7	713	708	707	724	723	723
ν_8	604	602	611	612	611	620
ν_9	335	322	329	337	336	-

are: ω_{CT1} = 3950 cm^{-1}, γ_{CT1} = 1900 cm^{-1}, μ^2_{CT1} = 6.37•10^{-58} C^2m^2 ω_{CT2} = 9820 cm^{-1}, γ_{CT2} = 3500 cm^{-1} and μ^2_{CT2} = 2.10•10^{-58} C^2m^2. From the crystal structure [3] one calculates: N_t = =1.19•10^{-27} m^{-3}, a_1 = 2.99 Å, a_2 = 3.03 Å . The ρ values extracted above from *ungerade* modes (0.14 and 0.93 for the central and external molecules, respectively) are used to estimate, by interpolation, the frequencies (ω_α and $\tilde{\omega}_\alpha$) of the totally symmetric modes in the absence of e-mv interaction. Rather than trying to extract the e-mv coupling constants from the spectral data, [19] we have preferred to use the g's independently determined for KTCNQ (Table II), only corrected for the frequency difference. [23] The only adjustable parameters are therefore the vibrational damping constants Γ_α which have been set for the best fit with the experimental IR spectrum; their values are reported in Table II. The calculated IR conductivity spectrum is compared with the experimental one in Fig. 1; the calculated and experimental Raman frequencies are reported in Table III.

The success of the above presented e-mv model in accounting for the e-mv perturbed spectral features of Cs_2TCNQ_3 is striking, considering the approximations of the model itself and the fact that the e-mv coupling constants have not been adjusted to improve the fit, but are just those extracted from KTCNQ. We only remark that there are some small differences between the calculated and experimental IR frequencies: they cannot of course be appreciated from Fig. 1, the largest one being 15 cm^{-1} (for the ν_3 mode). Moreover in Table III more than the precise frequency agreement between calculation and experiment (not particularly significant given the small e-mv shifts involved), one should look for the correct order of magnitude and direction of the shift, which is correct in most cases. In other words, the previously remarked apparently erratic behaviour of the a_g Raman frequencies (particularly of the ν_2 and ν_4 ones) is explained.

CONCLUSIONS

Apart from the achievement of a definite interpretation of the vibrational spectra of Cs_2TCNQ_3, the re-examination of the optical data of this old key compound has allowed us to reach several useful conclusions. First of all, we have introduced a model of e-mv interaction able to take into account the presence of both the inter-and intra-trimer CT states of trimerized segregated stack compounds. In terms of this model it has been shown for the first time that the a_g Raman frequencies of such compounds are perturbed by the e-mv interaction. This fact prevents their use for the determination of the charge residing on the molecular sites, which has to be determined from non-totally symmetric modes. In the case of Cs_2TCNQ_3 this charge turns out to be appreciably different from the so far assumed values of zero and one (0.1_4 and 0.9_3 for the centric and non centric molecules, respectively). Moreover, as the experimental data of Cs_2TCNQ_3 have been satisfactorily reproduced by using the e-mv coupling constants extracted from KTCNQ spectra, it has been demonstrated once more that these parameters are indeed transferable among different crystals.[10] Finally, the present work is a clear example of how the vibrational spectra can be reliably used to obtain detailed information on the electronic ground state of quasi one-dimensional organic CT crystals, provided that the perturbing effects of the e-mv interaction are properly accounted for.[20]

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