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## Electron–molecular vibration coupling in charge-transfer crystalline complexes

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**Abstract.** Analysis of the effect of the electron–molecular vibration (EMV) coupling on the conductivity spectra of charge-transfer crystalline complexes is presented. Discussion is limited to the case of *n*-merized compounds, for which the localized electronic states should be treated explicitly. Theoretical conductivity spectra based on the linear response and vibronic adiabatic Mulliken theories are compared with the experimental data. An alternative derivation of the linear response conductivity expression is presented. In addition, a simple method of calculation of the EMV coupling constants is proposed.

### 1. Introduction

In quasi-one-dimensional (Q-1D), highly conducting molecular solids the planar ion radical molecules stack to form conducting linear segregated chains. These charge-transfer (CT) molecular complexes create a unique opportunity for studies of intermolecular interactions. The overlap of electronic wavefunctions along the stacks greatly exceeds interstack coupling, and therefore sharp anisotropy may be expected. Indeed, reflectance is almost frequency independent when the electric vector of external radiation is perpendicular to the stacks, but for parallel polarization one observes an overdamped electronic CT band and a number of lines with half-width about  $100\text{ cm}^{-1}$  at frequencies close (but not equal!) to those of totally symmetric ( $a_g$ ) vibronic modes of isolated molecules. The qualitative picture of this phenomenon was clear from the very beginning: an external electric field parallel to the stack direction changes the electronic density on each molecule and, because the atomic equilibrium positions depend on molecular charge, the variations in the latter lead to intramolecular vibrations. For a non-degenerate valence electronic state the linear electron–molecular vibration (EMV) coupling constants are non-zero only for the  $a_g$  molecular vibrations.

However, a quantitative description seems far from complete. The main reason is the great variety of Q-1D CT crystals. The phase phonon theory of Rice and co-workers [1, 2] describes fairly well crystals with regular chains displaying metal-like conductivity. However, in the case of more localized electronic states, as happens in dimerized, trimerized and tetramerized compounds, electron correlations should be treated explicitly. The cluster model [3–7] seems to be more effective in these cases. Painelli and Girlando [8] showed that the linear response theory [3–7] and vibronic adiabatic Mulliken method [8, 9] give almost identical results in cases when vibronic lines do not overlap with the CT band.

The standard but rather tedious procedure to determine EMV parameters consists in fitting the appropriate theoretical expression to experimental reflectance or conductivity data. Several attempts have been made to offer alternatives. Firstly, an estimate of EMV coupling constants  $g_\alpha$  by a quantum chemical calculation for an isolated molecule was reported by Lipari *et al* [10]. Secondly, the differences between the bond lengths of neutral and charged molecules gave an independent estimate of  $g_\alpha$  [11]. Thirdly, all EMV parameters ( $g_\alpha$ , frequencies,  $\omega_\alpha$  and natural widths  $\gamma_\alpha$  of the originally uncoupled  $a_g$  modes) were determined from a plot of the real part  $\text{Re}[1/\sigma(\omega)]$  of the inverse complex conductivity [12]. This method works when one CT transition is much stronger than the others and also it is necessary to measure the reflectance in a very wide frequency range to ensure good quality of the Kramers–Kronig transformation. Fourthly, in cases when  $\omega_\alpha$  are much smaller than the frequency  $\omega_{CT}$  of CT excitation, EMV constants may be obtained from the positions of lines in Raman and IR spectra [9, 13].

In this paper we shall generalize the latter case so that the condition  $\omega_\alpha \ll \omega_{CT}$  no longer needs to be fulfilled and we shall discuss the conductivity spectra calculated with the linear response and vibronic adiabatic Mulliken methods.

## 2. Theory

In the cluster approach [3–6] the complex conductivity of Q-1D  $n$ -merized molecular semiconductors is obtained by superposition of linear responses of isolated  $n$ -mers ( $n = 2, 3, 4$ ) to an external electromagnetic field; the role of the interaction between  $n$ -mers was discussed in [7]. The microscopic model is defined by the following Hamiltonian:

$$H = H_e + H_v + \sum_{\alpha,i} g_\alpha n_i Q_{\alpha,i} - \mathbf{E} \cdot \mathbf{p} \quad (1)$$

where  $H_e$  and  $H_v$  are the Hamiltonians of the radical electrons and  $a_g$  intramolecular modes of vibration, respectively. Here,  $\hbar = 1$  is used for simplicity. The term radical here denotes the electrons transferred from donors to acceptors. Usually,  $H_e$  is taken in the Hubbard form with parameters  $U$  (on-site repulsion energy of two electrons with opposite spins) and  $t$  (transfer integral between the neighbouring sites) to describe the electronic correlations explicitly. EMV coupling is expressed by the third term in equation (1), where  $Q_{\alpha,i}$  denotes the normal-mode coordinate corresponding to the symmetric vibration  $\alpha$ , and  $n_i$  is the occupation number operator for the  $i$ th monomer. The last term in equation (1) describes the interaction of the electric dipole moment  $\mathbf{p}$  of the radical electrons with an externally applied electric field  $\mathbf{E}$ .

As shown in [3, 4] for dimers and in [5] for symmetric trimers, one can determine an IR-active antisymmetric combination of  $Q_{\alpha,i}$  and obtain the complex conductivity in the form

$$\sigma(\omega) = -i\omega N_d (e^2 A^2 / 4) [\chi_{CT}(\omega)^{-1} - D(\omega)]^{-1} \quad (2)$$

where

$$\chi_{CT}(\omega) = \sum_{\beta} \frac{2M_{\beta}^2 \omega_{\beta 1}}{\omega_{\beta 1}^2 - \omega^2 - i\omega\gamma_{\beta}} \quad (3)$$

$$D(\omega) = \sum_{\alpha} \frac{g_{\alpha}^2 \omega_{\alpha}}{\omega_{\alpha}^2 - \omega^2 - i\omega\gamma_{\alpha}} \quad (4)$$

Here,  $N_d$  is the number of  $n$ -mers per unit volume,  $A$  denotes the distance of CT ( $A = a$

for a dimer and  $2a$  for a trimer;  $a$  is the intermolecular spacing),  $M_\beta = \langle \beta | \delta n | 1 \rangle$  is the matrix element of the charge difference operator  $\delta n$  (equal to  $n_1 - n_2$  for a dimer and to  $n_1 - n_3$  for a symmetric trimer),  $\omega_{\beta 1} = E_\beta - E_1$ ,  $|\beta\rangle$  and  $E_\beta$  are eigenfunctions and eigenvalues of  $H_e$ , and  $\beta = 1$  labels the ground state.

The number of electronic excitations with the frequencies  $\omega_{\beta 1}$  depends on the kind of molecular organization in the stacks and on the stoichiometry. There is a single excited state in a dimer with one radical electron and  $\omega_{\beta 1} = \omega_{CT} = 2\sqrt{t^2 + \Delta^2}$ , where  $\Delta$  is the energy of monomer distortion due to cation influence enhanced by EMV coupling [4]. In a symmetric dimer with two radical electrons, only one CT transition with the energy  $\omega_{CT} = U/2 + \sqrt{U^2/4 + 4t^2}$  [3] is allowed. There are two allowed CT transitions in a symmetric trimer with two electrons, which roughly correspond to electronic transfers resulting in singly and doubly occupied monomers. For reasonable parameter values the latter transition can be ignored for the frequencies in the region of  $\omega_\alpha$  and only one term remains in equation (3). In the same way it is possible to find a dominant electronic CT excitation in the tetramerized compounds [6]. Thus, in all cases in the frequency range  $\omega \approx \omega_\alpha$ , equation (3) can be simplified as

$$\chi_{CT}(\omega) = 2M^2\omega_{CT}/(\omega_{CT}^2 - \omega^2 - i\omega\gamma_{CT}) \quad (5)$$

where  $\omega_{CT}$  denotes the frequency  $\omega_{\beta 1}$  of the dominant electronic excitation.

The frequencies of IR bands are obtained from the poles of  $\sigma(\omega)$ . The intramolecular vibrations are all coupled together through their common interaction with the CT excitation but, for an isolated vibronic band, which is well separated from the others, we can find the band frequency  $\Omega_\alpha$  from an analysis of the real part of  $\sigma(\omega)$ :

$$\Omega_\alpha = [(\omega_{CT}^2 + \omega_\alpha^2)/2 - \{[(\omega_{CT}^2 - \omega_\alpha^2)/2]^2 + 2M^2g_\alpha^2\omega_\alpha\omega_{CT}\}^{1/2}]^{1/2} \quad (6)$$

where the damping is neglected. For  $\omega_\alpha \ll \omega_{CT}$ , equation (6) can be reduced to the form found in [8]:

$$\Omega_\alpha = \omega_\alpha(1 - 2M^2g_\alpha^2/\omega_{CT}\omega_\alpha)^{1/2}. \quad (7)$$

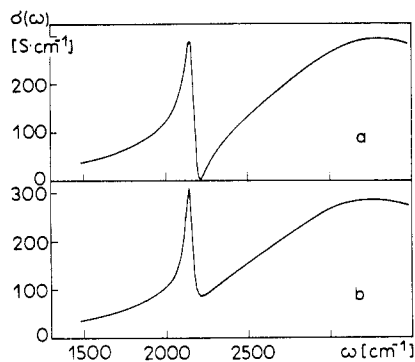
So, if the 'unperturbed' frequencies  $\omega_\alpha$  are determined (e.g. from the  $\text{Re}[1/\sigma(\omega)]$  spectrum [12]), one can calculate the EMV coupling constants  $g_\alpha$  from equation (6) if the positions of the bands in  $\text{Re}[\sigma(\omega)]$  are known.

Recently, a new expression for the complex conductivity of dimerized CT crystals has been offered in [8]:

$$\sigma(\omega) = -i\omega N_d \frac{e^2 A^2}{4} \chi_{CT}(\omega) \left( 1 + \sum_\alpha \frac{\Lambda_\alpha \Omega_\alpha^2}{\Omega_\alpha^2 - \omega^2 - i\omega\Gamma_\alpha} \right) \quad (8)$$

where  $\Omega_\alpha$  and  $\Gamma_\alpha$  denote the perturbed (i.e. those observed in IR conductivity spectra) frequencies of  $a_g$  vibrations and damping factors. The electronic CT polarizability is given by equation (3);  $\Lambda_\alpha$  can be found as the appropriate linear combinations of  $g_\alpha^2$  [8].

It has been shown by Painelli and Girlando [8] that the real part of the frequency-dependent conductivity given by equation (8) is virtually identical with that calculated from equation (2) for  $\omega_\alpha \ll \omega_{CT}$ . However, in most organic Q-1D semiconductors the CT band is situated at around  $3000 \text{ cm}^{-1}$  and this condition is not satisfied. Conductivity spectra calculated by the linear response method (equation (2)) and vibronic adiabatic Mulliken method (equation (8)) are shown in figures 1(a) and 1(b), respectively. The absolute values of  $\text{Re}(\sigma)$  correspond to the  $\text{MEM}(\text{TCNQ})_2$  salt [4]. It should be noted that the curves in figures 1(a) and 1(b) differ mostly in the high-frequency slope of vibronic  $\text{C}\equiv\text{N}$  band ( $\omega_2$ ), reflecting Fano resonance behaviour in the case of the linear response



**Figure 1.** Conductivity spectra calculated by (a) the linear response and (b) the vibronic adiabatic Mulliken methods, in the vicinity of the  $\text{C}\equiv\text{N}$  band. The absolute values of  $\text{Re}(\sigma)$  correspond to the  $\text{MEM}(\text{TCNQ})_2$  salt.

approach. We have tried the plots of other optical functions ( $\epsilon_1(\omega)$ ,  $\epsilon_2(\omega)$ , etc.) but no obvious advantages over  $\text{Re } \sigma$  plots that allow us to discriminate between the two theoretical approaches were found.

### 3. Discussion of the experimental results

Among the Q-1D CT molecular solids a vast group is formed by crystals with cluster-like chain structure. In particular, dimerized, trimerized and tetramerized salts are widely known. In these cases the tetracyano-p-quinodimethane (TCNQ) molecules or ions are grouped in the  $n$ -merized weakly interacting units with some localization of electronic states.

The TCNQ complex salts with N-methyl derivatives of pyridine (e.g.  $\text{NMePy}(\text{TCNQ})_2$ ,  $\text{NMe}_4\text{MePy}(\text{TCNQ})_2$  and  $\text{NMe}_{2,6}\text{MePy}(\text{TCNQ})_2$ ), with tetraethylammonium ( $\text{TEEA}(\text{TCNQ})_2$ ), with methylethylmorpholinium ( $\text{MEM}(\text{TCNQ})_2$ ) and methyl-N-ethylbenzimidazolium ( $\text{MNEB}(\text{TCNQ})_2$ ) as well as the simple salt of TCNQ with potassium ( $\text{K-TCNQ}$ ) can be considered as dimerized salts. In these and other similar salts the TCNQ are stacked plane to plane, in centrosymmetrically related pairs, approximately perpendicular to the stacking axis. There is favourable exocyclic-double-bond to quinonoid-ring overlap between adjacent molecules within each pair, but there is no direct overlap between the pairs. Within a pair, the mean perpendicular separation between the two TCNQ is a little smaller than the spacing between adjacent pairs [14]. The intradimer transfer integrals are usually ten times higher than the transfer integrals between adjacent pairs [15, 16].

The salts of TCNQ with caesium ( $\text{Cs}_2(\text{TCNQ})_3$ ) or S-methylthiuronium ( $(\text{MT})_2(\text{TCNO})_3 \cdot 2\text{H}_2\text{O}$ ) belong to the group of trimerized salts. The TCNQ molecules are stacked in groups of three with no direct overlap between adjacent triads. Usually, within the triads, two types of TCNQ unit are observed:  $\text{TCNQ}^0$  and  $\text{TCNQ}^-$  or  $\text{TCNQ}^{-\delta}$  and  $\text{TCNQ}^{\delta-1}$ . The salts with triethylammonium ( $\text{TEA}^+$ ), methyltriphenylphosphonium ( $\text{MTPP}^+$ ) or methyltriphenylarsonium ( $\text{MTPA}^+$ ) are structured with groups of four TCNQ with no direct overlap between adjacent tetrads. Usually, two types of overlap are observed within the tetrads. Therefore it is better to regard them as pairs of partially interacting dimers. The magnitude of the ratio of the intradimer to interdimer transfer integrals confirms that the interaction between dimers can be considered as weak. Of course, the charge distribution is not the same for both moieties of the TCNQ dimer [17].

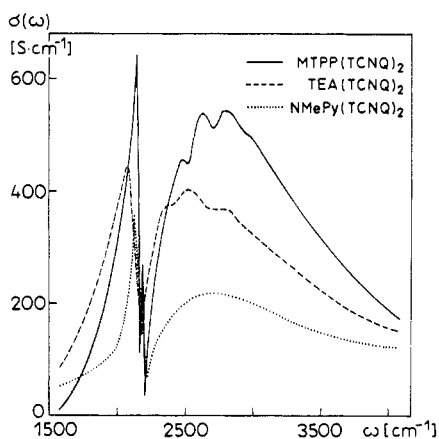
The polarized IR reflectivity of the above-mentioned  $n$ -merized TCNQ salts as well as others has been carefully studied by different investigators [4, 8–13, 18–30]. According

**Table 1.** Frequencies of the CT and  $\omega_2$  bands of the TCNQ salts.

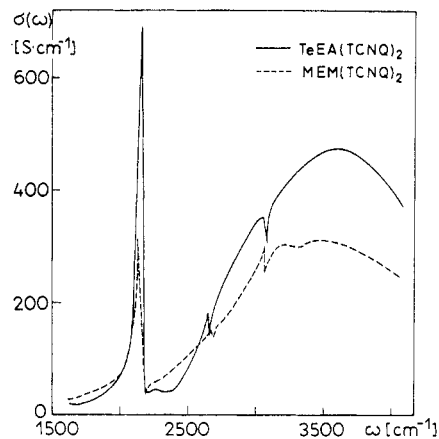
	Salt	$\omega_{CT}$ ( $\text{cm}^{-1}$ )	$\omega_2$ ( $\text{cm}^{-1}$ )
1	TEA(TCNQ) <sub>2</sub>	2500	2070
2	MNEB(TCNQ) <sub>2</sub>	2900	2155
3	(MT) <sub>2</sub> (TCNQ) <sub>3</sub> ·2H <sub>2</sub> O	3000	2115
4	MTPP(TCNQ) <sub>2</sub>	2800	2150
5	MTPA(TCNQ) <sub>2</sub>	2500	2100
6	NMe2,6MePy(TCNQ) <sub>2</sub>	2460	2090
7	NMe4MePy(TCNQ) <sub>2</sub>	2750	2155
8	NMePy(TCNQ) <sub>2</sub>	2600	2135
9	TeEA(TCNQ) <sub>2</sub>	3600	2150
10	MEM(TCNQ) <sub>2</sub>	3450	2150
11	Cs <sub>2</sub> (TCNQ) <sub>3</sub>	3550	2165

to current interpretations of the IR spectrum of TCNQ salts, it consists of a broad and strong electronic band at frequency  $\omega_{CT}$  and a series of relatively narrow lines ( $\omega_\alpha$ ) which are regarded as the  $a_g$  modes activated by means of the strong coupling with the electronic motion. A Kramers–Kronig analysis of reflection data with physically reasonable extrapolations is generally used to obtain the real part of the dielectric function  $\epsilon_1(\omega)$  and conductivity for IR frequencies  $\sigma(\omega) = \epsilon_0\omega\epsilon_2(\omega)$ . Availing ourselves of the above papers we were in a position to analyse the shape of the band at  $\omega_2 \approx 2200 \text{ cm}^{-1}$  attributed to the totally symmetric ( $a_g$ ) mode of the  $\text{C}\equiv\text{C}$  group stretching. This mode was chosen taking into account their intensity as well as localization near the CT band.

Parameters of both the CT and the  $\omega_2$  bands are given in table 1, whereas figures 2 and 3 show typical experimental conductivity spectra (from 1500 to 4000  $\text{cm}^{-1}$ ) of some selected salts. We note that the curves of figure 2 are highly asymmetrical. The high-frequency wings are more abrupt than their low-frequency counterparts. Such a behaviour of  $\sigma(\omega)$  near the totally symmetric modes of vibration proves that the resonance interactions of the vibrations with electronic systems occur for the  $\omega_2$  mode. The line



**Figure 2.** Experimental conductivity spectra of the salts well described by the linear response approach (experimental data are taken from [20, 22, 24]).



**Figure 3.** Experimental conductivity spectra of the salts not very well described by the linear response approach (experimental data are taken from [4, 31]).

asymmetry as well as a specific dip in the high-frequency slope of the vibronic  $\omega_2$  band testify to Fano resonance behaviour [32], typical in the case of the linear response approach (see figure 1(a) also). The same behaviour of the  $\omega_2$  band was observed for the salts 1–8 in table 1.

However, some  $n$ -merized TCNQ salts display a different spectral behaviour (figure 3). Salts 9–11 show a lack of pronounced Fano resonance behaviour and indicate that the linear response approach is not appropriate for these salts, in all respects. We agree with Painelli and Girlando [8] that the vibronic adiabatic Mulliken theory is more adequate for some salts, in particular for salts 9–11. Of course, this comparison of the data collected in table 1 does not solve the problem of which conductivity expression, equation (2) or (8), is more appropriate for describing the optical properties of  $n$ -merized molecular semiconductors. From the theoretical point of view we show in the final part of this section that the linear response theory result is more universal and can be reproduced within the framework of the vibronic adiabatic Mulliken approach as well. From the experimental viewpoint it is clear that more efforts are needed and we propose on the basis of figure 1 that more thorough IR investigations in the regions of the high-frequency wings of the  $a_g$  vibronic bands are needed.

Our approach not only describes the form of the band coupled to the CT band (e.g. the  $\omega_2$  band) but also permits us to propose a simple way of calculating the EMV coupling constants. From equation (6), one obtains

$$g_\alpha^2 = [\omega_{CT}^2 \omega_\alpha^2 - \Omega_\alpha^2 (\omega_{CT}^2 + \omega_\alpha^2) + \Omega_\alpha^4] / 2M^2 \omega_\alpha \omega_{CT}. \quad (9)$$

The parameter  $M^2$  is related to electronic excitations (see equation (5)) and can be either calculated theoretically [4–6] or estimated directly from experimental data. In the latter case we note that the peak value  $\sigma_1(\omega_{CT})$  of the CT band in the  $\text{Re}[\sigma(\omega)]$  spectrum does not depend appreciably on the EMV coupling; so we can neglect  $D(\omega)$  in equation (2) for  $\omega \approx \omega_{CT}$  and find that

$$\sigma_1(\omega_{CT}) = (N_d e^2 A^2 / 4) (2M^2 \omega_{CT} / \gamma_{CT}). \quad (10)$$

Finally, from equations (9) and (10) we obtain

$$g_\alpha = 7.793 \times 10^{-3} A \{ [\omega_{CT}^2 \omega_\alpha^2 - \Omega_\alpha^2 (\omega_{CT}^2 + \omega_\alpha^2) + \Omega_\alpha^4] / \omega_\alpha \gamma_\alpha \} [N_d / \sigma_1(\omega_{CT})]^{1/2} \quad (11)$$

where  $g_\alpha$  is expressed in reciprocal centimetres if  $\omega_\alpha$ ,  $\omega_{CT}$ ,  $\Omega_\alpha$  and  $\gamma_{CT}$  are also in reciprocal centimetres,  $N_d$  in reciprocal cubic centimetres,  $A$  in centimetres and  $\sigma_1(\omega_{CT})$  in siemens per centimetre. The EMV coupling constants calculated from equation (11), for K-TCNQ, are collected in table 2. The data used for the calculation originate from Painelli and Girlando [8]. For comparison, our values of EMV coupling constants found from equation (1), the EMV coupling constant used in the calculation of the vibronic spectrum of K-TCNQ by the vibronic adiabatic Mulliken model [8], and the EMV coupling constant found by a quantum chemical calculation for an isolated molecule [10] are also shown in table 2.

The agreement between the EMV coupling constants found from equation (11) and those obtained experimentally by Painelli *et al* [8] is rather good. Both series of data differ from the values calculated by Lipari *et al* [10] from quantum chemical evaluation, performed for the isolated TCNQ molecule.

In order to understand the difference between equations (2) and (8) we propose the following modification of the approach used in [8, 9]. The time-dependent electronic dipole moment  $\mu_{CT}(t)$  is generated by the external field  $E(t)$ :

$$\mu_{CT}(t) = \int_{-\infty}^t \varphi_{CT}(t-t') E(t') dt' \quad (12)$$

**Table 2.** The EMV coupling constants of K-TCNQ.

a <sub>g</sub> mode	g <sub>α</sub> (meV (cm <sup>-1</sup> ))		
	From [10]	From [8]	This paper
ω <sub>2</sub>	52.5	54	49 (397)
ω <sub>3</sub>	131.0	57	50 (405)
ω <sub>4</sub>	48.6	62	63 (506)
ω <sub>5</sub>	28.4	38	45 (364)
ω <sub>6</sub>	29.4	8	9.5 (77)
ω <sub>7</sub>	32.6	28	30 (242)
ω <sub>8</sub>	2.2	19	21 (172)
ω <sub>9</sub>	24.0	41	46 (372)

where  $\varphi_{CT}(t - t')$  is the purely electronic response function; its Fourier transform gives the electronic susceptibility (equation (3)). The total dipole moment  $\mu(t)$  is given by the sum of  $\mu_{CT}(t)$  and the dipole moment produced in the electronic system by intramolecular vibrations due to EMV coupling, where  $\mu$  itself acts as an external field on the molecular vibrations, which in turn acts as a surplus external field on the electrons:

$$\mu(t) = \mu_{CT}(t) + \int_{-\infty}^t \varphi_{CT}(t - t') dt' \int_{-\infty}^{t'} \varphi_V(t' - t'') \mu(t'') dt'' \quad (13)$$

So,  $\mu(t)$  is determined in a self-consistent way from equation (13) (compare with equation (B2) in [8]). Fourier transformation of equation (13), gives the following expression for the complex susceptibility:

$$\chi(\omega) = \chi_{CT}(\omega) + \chi_{CT}(\omega)\chi_V(\omega)\chi(\omega) \quad (14)$$

or

$$\chi(\omega) = \chi_{CT} / (1 - \chi_{CT}\chi_V) = (\chi_{CT}^{-1} - \chi_V)^{-1} \quad (15)$$

The latter result (15) coincides exactly with equation (2) obtained by standard linear response theory.

#### 4. Conclusions

We have examined two expressions proposed for the complex conductivity of  $n$ -merized Q-1D organic semiconductors by Rice and co-workers [2–4] and by Painelli *et al* [8]. So far no final decision has been reached in favour of any of these models on the basis of existing experimental data. Careful spectral measurements in the regions close to the high-frequency wing of a<sub>g</sub> vibronic bands are recommended.

A simple relation between the EMV coupling constant  $g_\alpha$  and the position of the corresponding vibrational band in the spectrum of the real part of the conductivity is obtained. The restriction  $\omega_\alpha \ll \omega_{CT}$  required by other workers is lifted in this paper. We propose the following way to extract  $g_\alpha$  from experimental data.

(i) Obtain the number of  $n$ -mers per unit volume and intermolecular separation distance from structural data.

(ii) Determine  $\omega_{CT}$ ,  $\sigma_1(\omega_{CT})$  and  $\gamma_{CT}$  as the position, peak value and half-width of the dominant electronic CT band, respectively.



(iii) Find  $\Omega_\alpha$  and  $\omega_\alpha$  as the frequencies of vibronic bands in  $\text{Re}(\sigma)$  and  $\text{Re}(1/\sigma)$  spectra, respectively.

(iv) Calculate  $g_\alpha$  according to equation (11).

The  $g_\alpha$ -values for K-TCNQ found in this manner agree with those obtained by a tedious fitting procedure.

Finally, a modification of the vibronic adiabatic Mulliken method is proposed and the expression obtained by Rice and co-workers is determined in the framework of the vibronic adiabatic Mulliken approach.

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