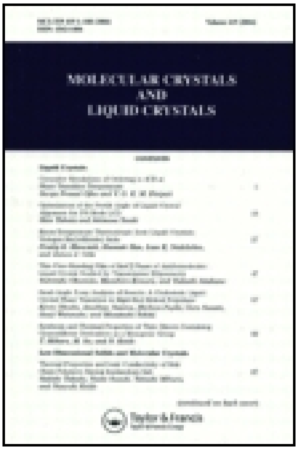

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Infrared Oscillator Strength Study of Charge Transfer in Two TCNQ Salts

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INFRARED OSCILLATOR STRENGTH STUDY OF CHARGE TRANSFER IN TWO TCNQ SALTS

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Abstract An attempt is presented here to deduce the mean charge, $\bar{q}$, transferred per TCNQ in either TCNQ salts or TCNQ composites, from an oscillator strength study of a particular IR bending mode which resonates at three distinct frequencies for TCNQ °, TCNQ$^-$ and TCNQ$^{-1/2}$.

IR absorption spectra of radical ion molecular solids based on the π electron acceptor tetracyanoquinodimethane (TCNQ) are very sensitive to the charge transferred and to the electron delocalization between molecular sites in the solid state. The shapes observed in the frequency range from 200 to 4000 cm^{-1} are dependent on the overlap between the large absorption band resulting from the electronic delocalization in accordance with the electric properties of the TCNQ salts and the internal vibrational modes of the individual TCNQ molecules. Due to this charge delocalization, most of the observed absorption bands are attributable to phase phonons which arise from the linear coupling of the underlying conduction electron molecular orbital to the ten totally symmetric a_g intramolecular vibrations of TCNQ,usually forbidden by the selection rules in the infrared [1].

We suggested in the past[2] that three close but well resolved peaks, at 863, 838-840 and 825 cm^{-1}, in the powder IR absorption spectra of TCNQ salts or of TCNQ composites, could serve as sensitive indicators of the presence in the material of TCNQ°, TCNQ$^{-1/2}$ and TCNQ$^-$, respectively. All these three peaks issue from the same TCNQ bending mode [2]. The intermediate one is the specific feature of an electron delocalized over, at least, the two TCNQ sites of a dimer $(TCNQ)^{-}_{2}$.

In another work[3], we also demonstrated that a considerable transformation of the powder IR absorption spectra of various TCNQ salts could be simply realized by repeatedly re-grinding and re-compacting the KBr pellet containing the material. On considering the general evolution of the three peaks at 863, 838-40 and 825 cm^{-1}, it could be concluded that this erosive process did not destroy individual molecules but introduced a progressive charge localization , according to :

$$(TCNQ)^{-}_{2} \longrightarrow TCNQ^{-} + TCNQ^{\circ}$$

Such an effect is especially important in the particular case of Cs_2 $TCNQ_3$, a salt which, according to its stoichiometry, has a mean charge per TCNQ monomer of $\bar{q}$ = 2e/3. Only two peaks, peaks A and B, at 825 and 838 cm^{-1}, are initially present, with almost equal intensities in the powder IR absorption spectrum of the salt. Under re-grinding and re-compacting of the KBr pellet, a significant transformation of the spectrum is obtained, involving a new and rapidly increasing contribution of the third peak at 863 cm^{-1}, peak C, representative of neutral monomers. A characteristic sequence of the various spectra so realised is shown in Figure 1.

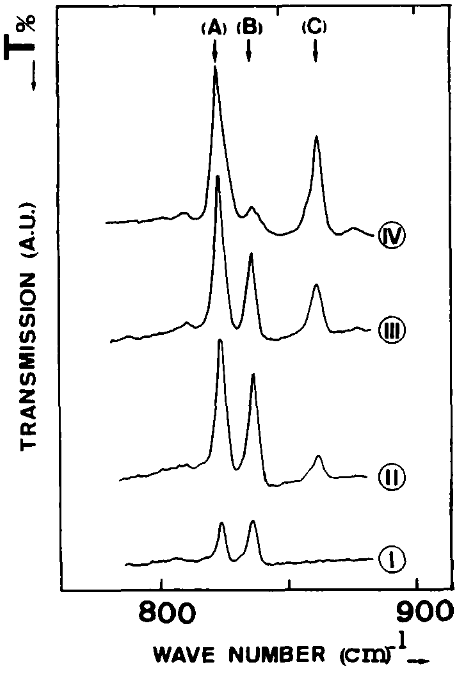

Fig. 1 : Powder absorption spectra of Cs_2 $TCNQ_3$
I) deposited on a KBr pellet
II) III) IV) relative evolution of the three peaks at 825, 838 and 863 cm^{-1} resulting from the recrushing of the KBr pellet I).

The integrated intensities I_A, I_B and I_C of the three peaks have been evaluated by a weight method, on each spectrum separately, in arbitrary units. It is clear, however, that only the normalized intensities are reliable from spectrum to spectrum. They are defined by :

$i_A = I_A/I$, $i_B = I_B/I$ and $i_C = I_C/I$, with $I = I_A + I_B + I_C$. They are reported in Figure 2 for several sequences, in the convenient form : i_A or i_C vs. $f(i_B)$.

From this figure, an approximation to a simple linear dependence is made quite plausible within the data accuracy. Thus, postulating for instance a linear relationship between i_B and i_C, in the form :

$i_C = a + b\, i_B$ (then, $i_A = (1 - a) - (1 + b)\, i_B$

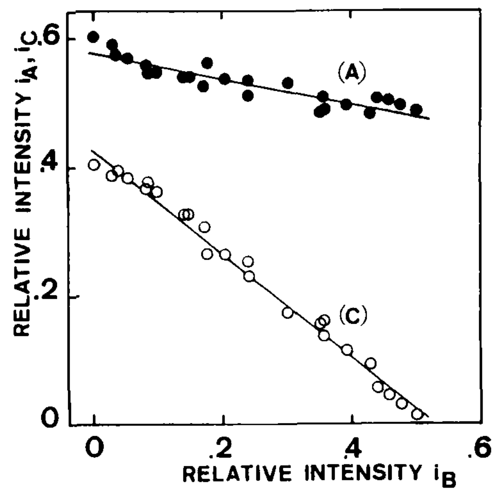

Figure 2 Linear dependence of the relative intensity of peak A (825 cm^{-1}) and C (863 cm^{-1}) versus the relative intensity of peak B (838-840 cm^{-1}) for Cs_2 $TCNQ_3$.

A linear least square fit of the data gives :

$a = 0.425$ $b = - 0.803$

with a correlation coefficient $|r|$ as high has 0.994.

A quantitative analysis of these data may be attempted on the basis of two hypotheses :

a) Constant number of TCNQ monomers in the treated pellet :

$$N_A + N_B + N_C = N = Cste$$

b) Constant total charge transferred to TCNQ monomers :

$$(N_A + 1/2\, N_B)\, e = N\bar{q} = Cste$$

Introducing now the respective oscillator strengths α, β, λ of peaks A, B, C, they may be quite generally defined by :

$$I_A = \alpha N_A \qquad I_B = \beta N_B \qquad I_C = \lambda N_C$$

One can then show, after a few steps,

$$a = \left(1 + \frac{\bar{q}/e}{1 - (\bar{q}/e)} x\right)^{-1}$$

$$b = -a \left(1 - \frac{0.5 - (\bar{q}/e)}{1 - (\bar{q}/e)} \frac{x}{y}\right)$$

with $x = \alpha/\gamma \quad y = \beta/\gamma$

and, from $\bar{q} = (2/3)e$ and the numeral values of and b, one gets finally :

$x = 0.676 \quad , \quad y = 0.381$

In order to check the overall reliability of this analysis, the same procedure has been applied to the case of another TCNQ salt, with a different stoichiometry : TEA $TCNQ_2$. The new normalized intensities are reported in Figure 3, in the same form as in Figure 2, which is :

i_A or i_C vs. $f(i_B)$

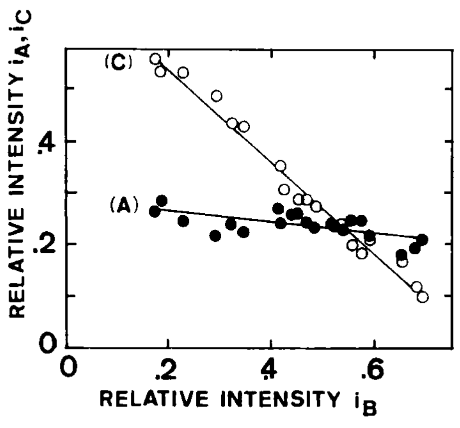

Figure 3 Linear dependence of the relative intensity of peaksA (825 cm^{-1}) and C (863 cm^{-1}) versus the relative intensity of peak B (838-840 cm^{-1}) for TEA $TCNQ_2$.

On the assumption that the oscillor strengths α β and γ, and, also x and y, are left unchanged from salt to salt, the only parameter allowed to vary is then the mean charge $\bar{q}$ transferred per TCNQ monomer. It may be numerically deduced from the relation :

$$\frac{\bar{q}}{e} = \frac{N_A + (N_B/2)}{N} = \frac{u + (v/2)}{1 + u + v}$$

with

$$u = \frac{1}{x}\,\frac{i_A}{i_C}, \qquad v = \frac{1}{y}\,\frac{i_B}{i_C}$$

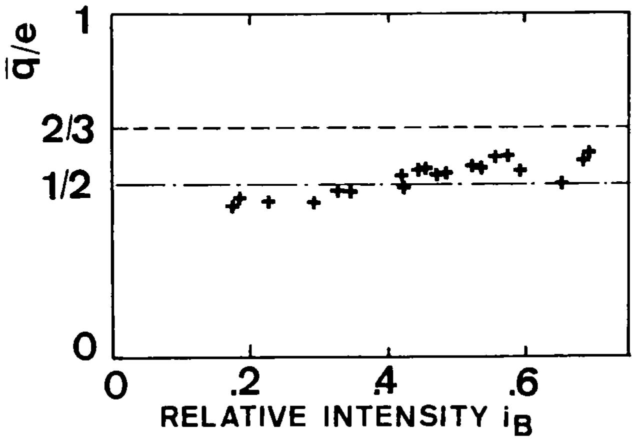

Figure 4 Computed mean charge $\bar{q}$ transferred per TCNQ monomer in TEA $TCNQ_2$ versus the relative intensity of peak B (838-840 cm^{-1})

The results of this approach are reported in Figure 4. They may be directly compared to the theoretical value of $\bar{q} = 0.5$ e which is expected for the case of TEA $TCNQ_2$. It may be concluded from the results of fig. 4 that the present agreement is only semi quantitative. The decreasing character of the experimental $\bar{q}$ values versus i_B might indicate that the starting hypotheses are not entirely correct. Further work is necessary to elucidate this point.

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