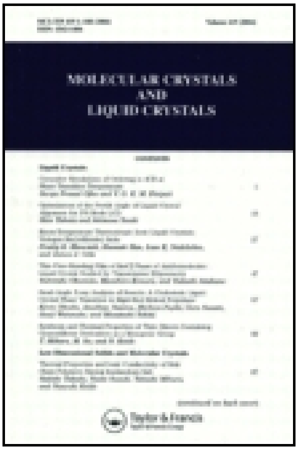

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Electronic and Vibrational Absorption Spectra of Radical Cation Salts Based on TTF Derivatives

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ELECTRONIC AND VIBRATIONAL ABSORPTION SPECTRA OF RADICAL CATION SALTS BASED ON TTF DERIVATIVES

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ABSTRACT Electronic and vibrational absorption spectra of radical cation salts based on TMTTF and unsymmetrical related molecules have been studied.
A quantitative approach of the charge transfer absorption band has allowed the authors to propose a DRUDE-LORENTZ model to fit the experimental data. The physical meaning of the parameters associated with this fit is based upon the presence of strong electron-electron interactions in a narrow electronic band model ("extended HUBBARD model") in agreement with the other physical properties known in these compounds.

INTRODUCTION

A considerable current interest is devoted to the bonding and the properties of mixed valence systems; among these the π ion-radical salts formed with segregated stacks of planar molecules are organic conductors characterized by unique electronic, magnetic and optical properties (1). In such materials, exhibiting a partial ionic ground state, the electrons behave as if they were confined to move in only one or two directions. This restricted electronic dimensionality gives rise to a large variety of peculiar physical situations which have aroused a great deal of interest. The electronic properties therefore have been largely explored, nevertheless the spectroscopic features are also unusual and characteristic of these new materials. In particular, concerning the optical elementary excitations, these compounds are characterized by charge transfer excitations at a smaller energy than any intramolecular one of FRENKEL's type (2).

Two types of charge transfer (C.T.) bands have been recognized, labelled A and B for a partially and a completely ionized salt, respectively (3). These C.T. transitions, which are polarized along the stacking axis, occur for excitation energy situated around 1eV and below whereas the classical intramolecular transitions, with a different polarization, are observed only above 1,5 - 2 eV (3). Besides, A bands originate charge tranfer induced IR vibrational absorptions which are normally IR inactive. To understand this effect the role of the electron-molecular vibrational (e-mv) coupling has been recognized ; this is known as the vibronic model (4).

These C.T. transitions are characteristic of the different interactions present both in the solid and the molecular entities. The optical experiments are valuable tools for understanding the presence of a given electronic ground state (insulating, conducting, superconducting or antiferromagnetic.

In this investigation our goal has been to investigate the spectroscopic properties of two new series of radical cation salts which present a similar structural organization as the already known TMTTF (tetramethyltetrathiafulvalene) salts. We will present, in the next part, these different compounds. We will then describe the experiments based on absorption measurements and finally, in a last part, we will propose a quantitative approach to give an account of these new results using an HUBBARD type model.

THE COMPOUNDS : A GENERAL PRESENTATION.

The investigated compounds are on the one hand already well known TMTTF salts (1) and on the other hand two new series of salts based on unsymmetrical TTF derivatives : trimethylenetetrathiafulvalene (tTTF) and dimethyltrimethylenetetrathiafulvalene (DMtTTF) (see Table I). These molecules form 2 - 1 stoichiometric phases with a wide variety of monovalent anions using a classical electrooxidation single crystal growing process. They all present a similar structural organization which is characterized by:

- segregated stacks of organic molecules organized in "zig-zag" mode along the a axis and in sheets along the b direction ,
- the anions are positionned in cavities formed between these chains (c direction). According to their symmetry they are classified into two groups ; if they are non-centrosymmetric they can be ordered either during their formation or when the temperature is lowered (order-disorder phase transition at T_{OD}) this counter-ion ordering is characterized by a given superstruture of the original lattice cell. These main structural characteristics are summarized in Table I.

Concerning the physical properties, an overview is also given in the Table I. Room temperature values for the electrical conductivity, measured along the stacks ($\sigma_{\parallel}$) show that they are moderate conductors. The best ones are the DMtTTF salts (11). Almost all of them present a rather strong paramagnetism (χp) which can be due to electron-electron interactions.

Finally in these salts we are in the presence of a competition between a periodic lattice distortion (PEIERLS type) and a magnetic order at low temperature (occuring at Tc) which is

Compounds and References	Structural Characteristics				Physical Properties			
	Space Lattice	Organic Stacks	Anion ring, Phase transition T_{OD}	Super-structure	R.T. Conductivity (σ Ω^{-1} cm^{-1})	Paramagnetism χ_p (10^4 emu CGS $mole^{-1}$)	Phase transition implying stacks	Ground State
$(TMTTF)_2$ SCN (5)	Triclinic	Dimers	T_{OD} = 160 K	(a,2b,2c)	20 - 30	6,60	Tc = 9 K	AF^{++}
$(TMTTF)_2$ SbF_6 (6)			-	-	10	6,90	Tc = 6 K	AF
$(TMTTF)_2$ ReO_4 (7)			T_{OD} = 160 K	(2a,2b,2c)	20 - 30	-	-	I^{++}
$(tTTF)_2$ BF_4 (8)	Triclinic	Tetramers	ordered anions	(a,2b, c)	0.3-1, SC^{++} (ΔE = 0.1eV)	2.65	-	I
$(tTTF)_2$ AsF_6 (8)		Dimers	-	-	20 - 30	6.20	Tc = 55 K (PLD ?)$^{+++}$	I
$(DMtTTF)_2$ AsF_6 (9) (10)	Triclinic	Dimers	-	-	80	5.70	Tc = 10 K	AF
$(DMtTTF)_2$ ClO_4 (11)	Monoclinic	regular	ordered anions	(a,2b, c)$^{+}$	250	6.40	Tc = 7 K	AF

+ equivalent superstructure in a triclinic lattice

++ AF : antiferromagnetic; I : insulator; SC : semiconductor

+++ PLD: Periodic Lattice Distortion

TABLE 1: Main structural and physical characteristics of the investigated radical-cation salts.

governed by a subtle balance between different interactions. The understanding of these interactions is a fundamental point for the low-dimensional systems and one way to improve it is the investigation of the electronic and vibrational absorption spectra.

EXPERIMENTAL TECHNIQUE AND RESULTS.

Comparative transmission measurements of finely ground KBr pellet samples with a weight concentration (C%) smaller than 1% have been done. This routine technique, which needs a careful procedure, has been already used for IR experiments on the TMTTF salts (12). It just needs polycristalline samples in small amounts to determine the spectra. However the absorption spectrum, which resembles the absorption coefficient of single crystals, is an averaged value over all directions. In these materials of low crystal symmetry (triclinic and monoclinic, see Table I) the response of the medium is characterized by a tensor dielectric function (13).

Taking into consideration previous work, we will consider only a mean value which corresponds to one component of this tensor associated with the privileged electronic direction Furthermore, thanks to the attribution of C.T. bands using polarized light, we will use the same terminology as already described in the introduction (3).

The experiments have been carried out over most of the optical range using I.R. (350-4800cm^{-1}) and visible-U.V. spectrometers (3800-25000cm^{-1}).

The results obtained for the two new series of compounds are presented Figures 1 and 2.

i) The IR absorption spectra are similar to those observed for TMTTF compounds (12)(Figure 1). A large and

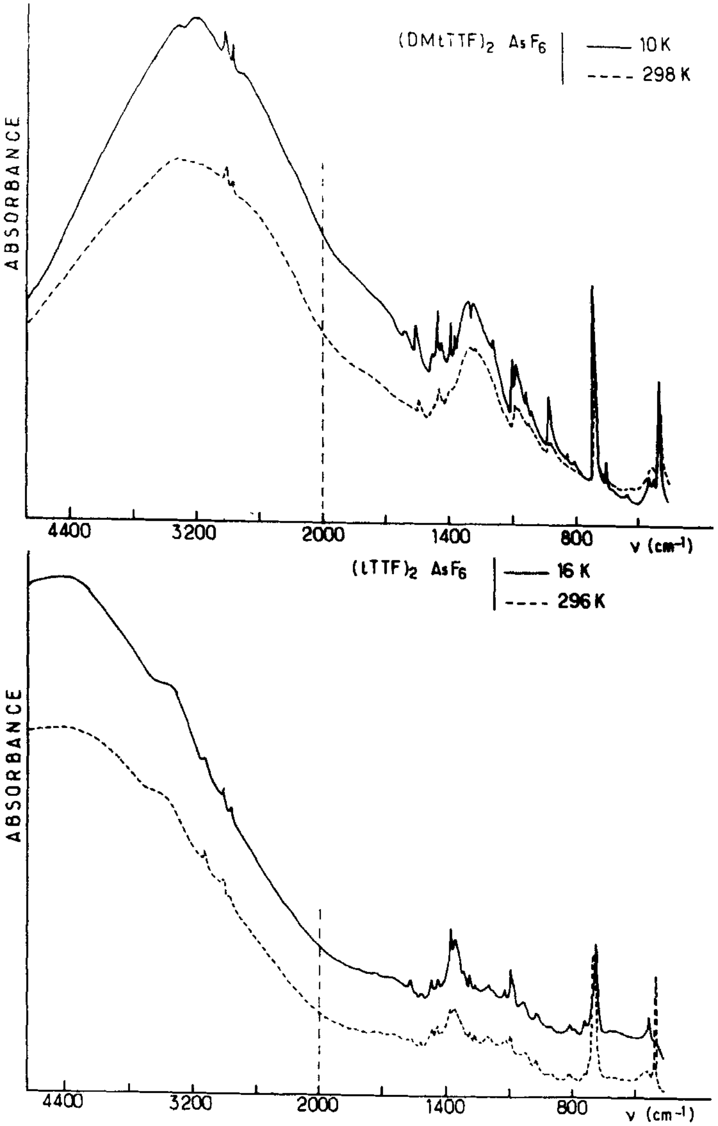


FIGURE 1 : Room temperature (broken curve) and lowest temperature (full curve infrared absorption spectra between 4800 and 400 cm^{-1} of (DMtTTF)$_2$AsF$_6$ and (tTTF)$_2$AsF$_6$ (The scale above 2000 cm^{-1} is twice the scale used below this wave number.

broad electronic band is present at high frequencies. This is the A peak characteristic of mixed valence compounds (3). On the tail of this electronic band the vibrational absorption lines are superimposed. The most intense lines are attributed to the vibronic lines as in TMTTF salts ($\nu_4 \equiv \nu_{C=C}$ central and $\nu_{10} \equiv \nu_{C=S}$ internal). Their characteristics however are dependent on the lack of symmetry of these molecules and is currently under investigation.

ii) The electronic absorption bands have only been fully investigated at room temperature, but we know from the I.R. spectra that the A band is weakly T.dependent (see Figure 1). Besides, we have neglected the vibrational absorption lines which have been removed from the tails of the C.T. bands. The results are presented Figure 2 for the three series of investigated salts. Firstly, we observed an intense C.T. A band below 1eV, the position of which changes slightly for the different compounds, and secondly, around and above 2eV, we observed the intramolecular excitation bands (C and D peaks (3)).

These last absorption bands are not relevant to our investigation. More significantly the C.T. B band is almost absent or hidden by the base-line.

This B peak has been observed in TTF salts (3) and is present at 1.3eV for a completely ionized TMTTF salt (14). In these mixed valence compounds, the only C.T. excitation is due to an electron jump to the next neighbouring molecule with a different valence state :

$$\ldots\ D^+\, D^0\, D^+ \ldots \xrightarrow{Ect} \ldots\ \overset{\curvearrowright}{D^0\, D^+}\, D^+ \ldots$$

We can consider therefore that almost all the oscillator strength of the electrons is concentrated in this localized excitation for which we will try to afford some explanation.

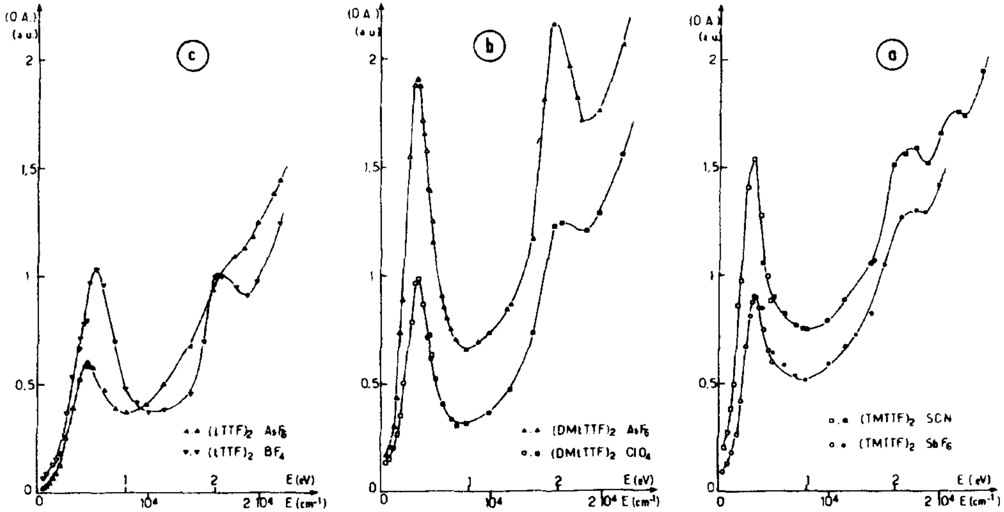


FIGURE 2 : Room temperature optical absorption (O.A.) spectra in I.R. (o,□,Δ,∇ and visible - UV range (●,■,▲,▼) for respectively :
a) TMTTF salts (C = 0.173 % for SCN and C = 0.07 % for SbF$_6$ salts)
b) DMtTTF salts (C = 0.14 % for ClO$_4$ and C = 0.22 % for AsF$_6$ salts)
c) tTTF salts (C = 0.041 % for BF$_4$ and C = 0.0026 % for AsF$_6$ salts)

DISCUSSION AND ANALYSIS

1. A Quantitative Approach

From these C.T. (A) absorption lines much information can be extracted about the shape of the absorption band, assumed to be homogeneous, the position of the maximum and its intensity.

It seems very worthwhile to undertake a quantitative approach and therefore to calculate the mean absorption coefficient (α) we have assumed that the pellet samples behave as an homogeneous medium for these very dilute compositions (15) :

$$\alpha = \frac{2.303\ A}{\Phi\ e} \qquad (1)$$

where A is the absorbance, e the sample thickness and Φ the volume fraction of the compound in KBr.

Using (1) we have calculated the energy dependence of the absorption coefficient with a relative accuracy estimated to be about 20-25% (Figure 3).

Now, to fit these absorption lines, we have chosen a DRUDE-LORENTZ model in agreement with the previous investigators (3).

The complex dielectric function $\epsilon(\omega)$ and the absorption coefficient $\alpha(\omega)$ are (13)

$$\epsilon(\omega) = \epsilon_1(\omega) + i\ \epsilon_2(\omega) \qquad (2)$$

$$\text{with } \epsilon_1 = \epsilon_\infty + \frac{\omega_p^2\ (\omega_1^2 - \omega^2)}{(\omega_1^2 - \omega^2)^2 + \Gamma^2\omega^2}$$

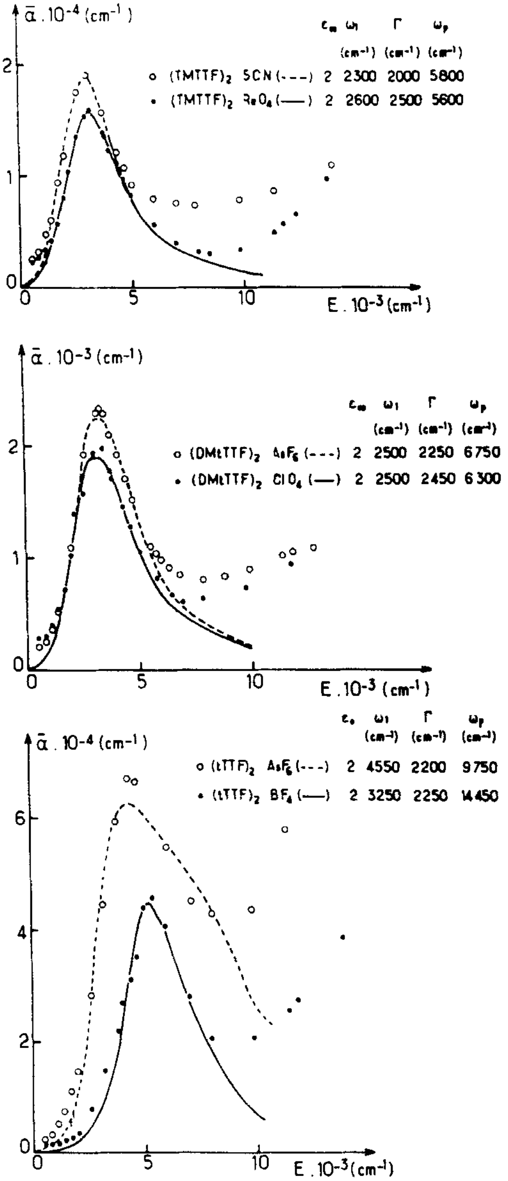


FIGURE 3 : Absorption spectrum of powdered samples of TMTTF (a), DMtTTF (b) and tTTF (c) salts. The lines are a fit to the data given by the experimental points using equation (3) in the text ($\overline{\alpha}(\omega) = 1/3\ \alpha(\omega)$. The parameters of the best fit are given on the Figures.

$$\epsilon_2 = \frac{\Gamma.\omega.\omega_p^2}{(\omega_1^2 - \omega^2)^2 + \Gamma^2\omega^2}$$

$$\text{and } \alpha(\omega) = \frac{\omega.\epsilon_2(\omega)}{C.n(\omega)}$$

$$\text{with } n(\omega)^2 = 0.5 \left\{ \epsilon_1^2(\omega) + \epsilon_2^2(\omega)^{1/2} + \epsilon_1(\omega) \right\} \quad (3)$$

Where the parameters are :

- ϵ_∞ : the core dielectric constant
- ω_p : the plasmon frequency
- ω_1 : the characteristic resonance frequency
- Γ : the fullwidth at half-maximum for the Lorentz oscillator.

An usual fitting procedure was done after selecting a reasonable value for the core dielectric constant (16)(17). On Figure 3, we observe that in the frequency range 1 - 7 (10^3cm^{-1}) a good agreement between experimental points and the calculated curves is obtained for the given set of parameters (see Table 2).

To check the validity of such an approach we have done I.R. and visible reflectivity measurements (R) on a polycristalline sample of $(TMTTF)_2$ SCN. We have compared the experimental reflectivity, after substracting the vibrational component, and the calculated one using a constant value for the transverse reflectivity terms (17), equation 2 and the indicated parameter values (Figure 4). The quantitative agreement is correct and, more significantly, there is a good coïncidence for the two maximum values around 2200cm^{-1}. This result has encouraged us to pursue the model analysis.

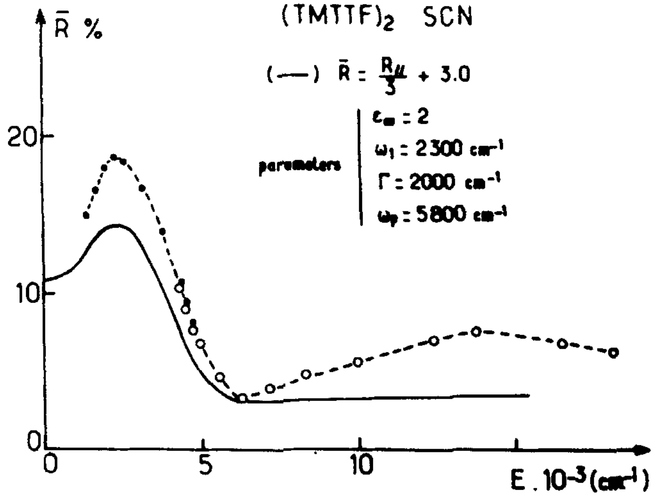


FIGURE 4 : Plots (o,•) of the room temperature reflectance of a polycristalline sample of (TMTTF)$_2$SCN. The full line is the mean reflectivity value $\bar{R}$ with the given parameters.

2. The Electronic Band Description

The DRUDE-LORENTZ model approach needs to develope the physical meaning of these different parameters. Our picture is based upon an energy band model including strong electronic correlations as described by HUBBARD (18).

In these narrow electronic band systems it is well known that it is necessary to go beyond the free electron gas approximation to explain the physical properties, i.e. to include both electron-phonon and electron-electron interactions. The former, which is evidenced by the presence of vibronic lines, can be quantified using the linear response theory as proposed by RICE and coll. (4) for the dimer model.

A perturbation of the dielectric function (cf eq. 2) is introduced which depends upon the e-mv coupling strength.

It turns out that this is a weak perturbation in derivative TTF compounds which can be neglected, in a first approximation (17)(19), compared to the electron-electron interactions (20).

The electronic description of these π molecular solids is governed by the following parameters inside a 1d picture :

- $t_{\parallel}$ is the transfer integral along the stacks. In the tight-binding model for an uniform stacking the bandwidth (Δ) is equal to $4t_{\parallel}$,
- The COULOMB interactions between charge carriers are introduced through on site correlations (U) and the adjacent site correlations (V) (18).

This is an extended HUBBARD model for which no general solution for finite values of these parameters exist (21). A schematic band representation is given Figure 5. For these compounds with a 2-1 stoichiometry and neglecting the weak intrastack dimerization, for a free electron gas we are in presence of 3/4 filled band. Following now, MAZUNDAR and SOOS (20) in the large U and V approximation we will observe a successive band splitting with U and V. The basic conduction band is decomposed into four HUBBARD subbands. At absolute zero and inside the atomic limit $t_{\parallel} = 0$, when there is only one electron on each molecular orbital, we will have the three lower subbands occupied while the upper one is empty. A direct interband transition will imply an energy equal to V - 2t (20). Therefore at room temperature the observed electronic band transition will need an energy of about V, the nearest neighbour correlation energy.

Compounds	Optical Parameters		
	$\omega_p\,(cm^{-1})$; $t_\parallel$ (eV)	$\omega_{CT}(cm^{-1})$: V(eV)	$\Gamma(cm^{-1})$: $t_\parallel$ (eV)
$(TMTTF)_2$ X	5800 – 5600 < 0.15 [16] < 0.20 [17]	2500 ~ 0.30	2000 – 2500 > 0.12
$(DMtTTF)_2$ X	6700 – 6500	2300 ~ 0.28	2300 > 0.14
$(tTTF)_2$ X (+)	14500	3200 ~ 0.40	2200 > 0.14

(+) except for $X = BF_4$ which presents an energy gap $\Delta E \simeq 0.1$ eV

TABLE 2 – OPTICAL CONSTANTS AND DEDUCED ELECTRONIC BAND PARAMETERS.

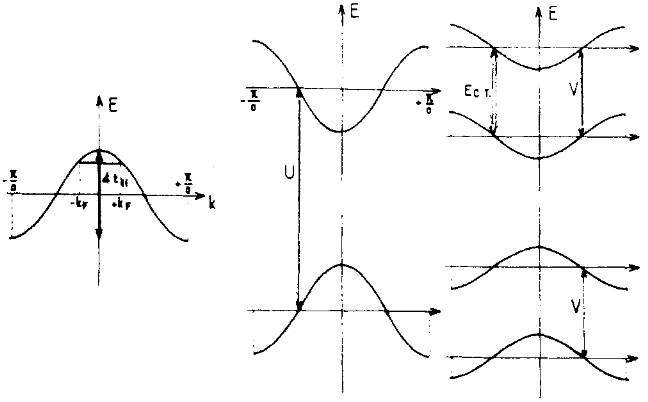
From this picture we are able to give the physical meaning of the parameters used in this LORENTZ oscillator model (see Table 2) :

i) ω_1 is the transition frequency between two electronic states separated by the C.T. energy ($\hbar\,\omega_{CT} \equiv \hbar\,\omega_1$). For these narrow energy bands therefore : $\hbar\,\omega_{CT} \geqslant V$.

ii) The observed line width (Γ) may reflect both band and life time contributions (22). We can assume that Γ gives the lower acceptable values for the bandwidth : $\hbar\,\Gamma > 2t_\parallel$.

iii) The plasmon frequency (ω_p) is related to the oscillator strength (f) and the intensity of the absorption band (13). If we introduce the plasmon frequency value in DRUDE'S model (ω°_p) it follows that (19):

$$f = \frac{m^*}{4\,\pi e^2 N}\,\omega_p^{\,2} = \frac{\omega_p^{\,2}}{(\omega^\circ_p)^2} < 1$$



1d tight-binding model (uniform stack) 3/4 filled band (for p = 0.5)

$E = 2|t_\parallel| \cos ka$

HUBBARD subbands for one-site correlation energy U

$U > 4|t_\parallel|$

splitting of the HUBBARD subbands with nearest neighbours correlation energy V

$V > 2|t_\parallel|$

FIGURE 5 : Schematic band representation for an extended HUBBARD model in the large U approximation : $U > 2V > 4\ t_\parallel$ (from MAZUMDAR and SOOS (20))

When using the free electron gas model ($\omega_1 \equiv \omega_{CT} \equiv 0$) to fit the reflectivity minimum we will obtain an overestimated value for $t_\parallel$ as indicated in Table 2 in TMTTF salts. This value is nevertheless in agreement with the estimate obtained from the linewidth parameter.

We finally get some approximate values for V and $t_\parallel$ (Table 2). Furthermore in order to obtain a magnetic ground state (see Table 1) it is usually accepted that it is necessary to have $U > 2V$ favorable for spin density waves (21).

Therefore :

$$U\ (> 1\text{eV}) > 2V(0.6 - 0.8\text{eV}) \geqslant \Delta = 4t_\parallel(0.5 - 0.7\text{eV}).$$

As far as we neglect the transverse interactions in this 1d extended HUBBARD model the interpretation of these optical experiments furnishes a classification of these parameters ($U > V \geqslant t_\parallel$) neglecting the electron-phonon interactions.

The presence of large COULOMB interactions is in qualitative agreement with the observation of an enhanced paramagnetism and a moderate electrical conductivity (1)(16).

CONCLUSION

A quantitative approach to the electronic absorption complements the reflectivity measurements. We have shown that a classical DRUDE model is not sufficient for these narrow band materials and we have proposed that the electronic excitations are related to strong electronic correlations following previous work done by TORRANCE and Coll. (3) and MAZUNDAR and SOOS (20) respectively. The C.T. "A band" is a single particle transition localized on neighbouring sites which is more or less insensitive to the detailed crystal structure but rather characteristic of the involved molecular blocks (Table 2).
The fit using a LORENTZ oscillator conducts us to the following concluding remarks :

i) At low frequencies, the experimental electronic absorption is always above the calculated values (Figure 3) because the DRUDE-LORENTZ model will always lead to a null d.c. conductivity in contradiction with the experimental findings (see Table 1). Temperature dependence investigations are necessary to explain this point.

ii) The characteristic resonant frequency (ω_{CT}) which is found, is not equal to the maximum of the absorption band (see Figure 1) but rather is determined by the reflectivity maximum (see Figure 4).

iii) The vibronic effect which is a charge transfer induced vibrationnal absorption in mixed valence compounds appears to be present in these new compounds based on unsymmetrical molecules. A detailed experimental study is under investigation, nevertheless it already appears that

RICE's dimer model (4) would not be sufficient to explain these results.

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