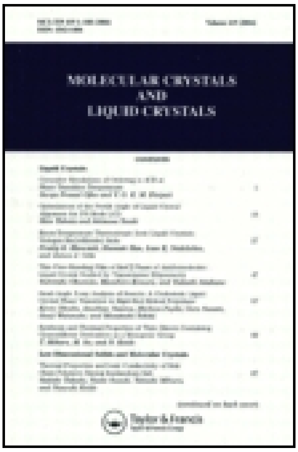

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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To cite this article: R. σwietlik & V. M. Yartsev (1993): Infrared Spectra of Quasi-One-Dimensional Semiconductors with Tetramerized Stacks, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 229:1, 135-140

To link to this article: http://dx.doi.org/10.1080/10587259308032187

Mol. Cryst. Liq. Cryst. 1993, Vol. 229, pp. 135–140
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Printed in the United States of America

INFRARED SPECTRA OF QUASI-ONE-DIMENSIONAL SEMICONDUCTORS WITH TETRAMERIZED STACKS

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Abstract Fine structure of vibronic bands in powder absorption and single crystal reflectivity spectra is investigated for a series of tetramerized TCNQ ion-radical salts. The origin of this fine structure is discussed.

INTRODUCTION

The various cations and TCNQ (tetracyanoquinodimethane) form many ion-radical salts with tetramerized TCNQ stacks, i.e. the molecules are grouped in tetramers ...ABBA..ABBA..., with two radical electrons residing on each tetramer. A significant overlap of π molecular orbitals exists inside the tetramer, whereas the interaction between tetramers is considerably weaker. It is well known that infrared spectra of TCNQ salts are mainly determined by the coupling of electrons with totally symmetric intramolecular vibrations of TCNQ (a_g modes)[1]. An interesting feature of the infrared spectra of tetramerized TCNQ salts is the presence of specific fine structure of a_g bands: the bands are doublets. In each doublet one can distinguish the wide (linewidth up to 100 cm^{-1}), relatively strong component of lower frequency and the narrow (linewidth between 10 and 20 cm^{-1}), relatively weak component of higher frequency. The narrow components exhibit stronger temperature dependence and in some salts with higher conductivity are not observed at room temperature.

The aim of this paper is the discussion of EMV coupling phenomena in TCNQ salts with tetramerized stacks with special attention to the origin of a_g bands splitting. For this reason we have performed infrared studies of a series of salts with different organization of conducting stacks, i.e. different degree of isolation of neighbouring tetramers. We have studied 1:2 complex TCNQ salts with the following cations: TEA (triethylammonium), MTPP (methyltriphenylphosphonium), NPrQn (N-propylquinolinium), PrPht (N-propylphtalazinium), PrQuin (N-propylquinoxalinium). The spectra of TEA(TCNQ)$_2$, MTPP(TCNQ)$_2$ and NPrQn(TCNQ)$_2$ are already well known from the literature[2-7], whereas the spectra of PrPht(TCNQ)$_2$ and PrQuin(TCNQ)$_2$ have never been published before. In Table I we present the dc conductivity σ at room temperature and activation energy E_a together with the values of transfer integrals t calculated from crystallographic data of the investigated salts[8-15].

TABLE I

SALT		σ(300K) S/cm	E_a eV	t_{AA} eV	t_{AB} eV	t_{BB} eV
TEA(TCNQ)$_2$	T=295K	7	0.12	0.11	0.15	0.11
NPrQn(TCNQ)	T=300K	1	metallic	0.08	0.14	0.13
	T=100K	-	0.46	0.04	0.18	0.18
PrPht(TCNQ)$_2$	T=300K	1.9×10^{-2}	0.29	0.07	0.15	0.12
PrQuin(TCNQ)$_2$	T=300K	1.6×10^{-2}	0.24	-	-	-
MTPP(TCNQ)$_2$	T=300K	1.4×10^{-3}	0.43	0.03	0.15	0.14
	T=326K	-	0.33	0.04	0.14	0.12

EXPERIMENTAL AND RESULTS

We have measured powder absorption spectra of TEA(TCNQ)$_2$ NPrQn(TCNQ)$_2$, PrPht(TCNQ)$_2$, PrQuin(TCNQ)$_2$ and MTPP(TCNQ)$_2$ at temperatures 296 K and 86 K in the frequency region 400-4000 cm^{-1} using the grating spectrophotometer Perkin-Elmer 577. The samples for absorption measurements were prepared by compressing the finely powdered salts with KBr at weight ratio 1:1000. The single crystal reflectivity spectra of NPrQn(TCNQ)$_2$ and PrPht(TCNQ)$_2$ were measured in polarized light at room temperature (300-4000 cm^{-1}). Some supplementary measurements of powder absorption spectra were carried out at room temperature using FT-IR Perkin-Elmer 1725X spectrometer within the range (400-7200 cm^{-1}). For comparison and discussion we have taken into account the results of our earlier measurements of MTPP(TCNQ)$_2$[5,6] and the literature data for TEA(TCNQ)$_2$[2-4] and NPrQn(TCNQ)$_2$[7].

The reflectivity spectra of PrPht(TCNQ)$_2$ single crystals for two

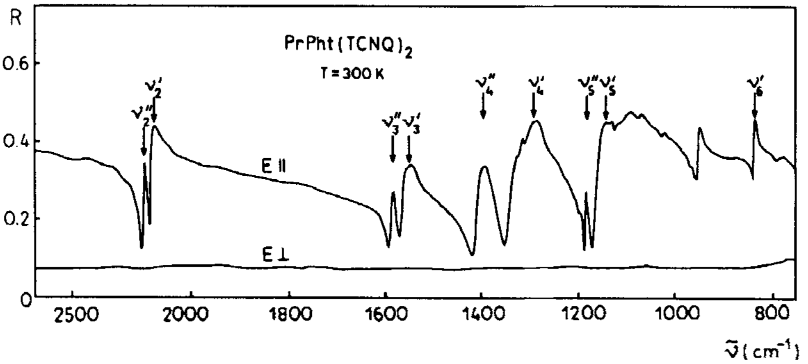

FIGURE 1 Infrared reflectivity of $PrPht(TCNQ)_2$ single crystals for polarization parallel (E ∥) and perpendicular (E ⊥) to TCNQ stacks.

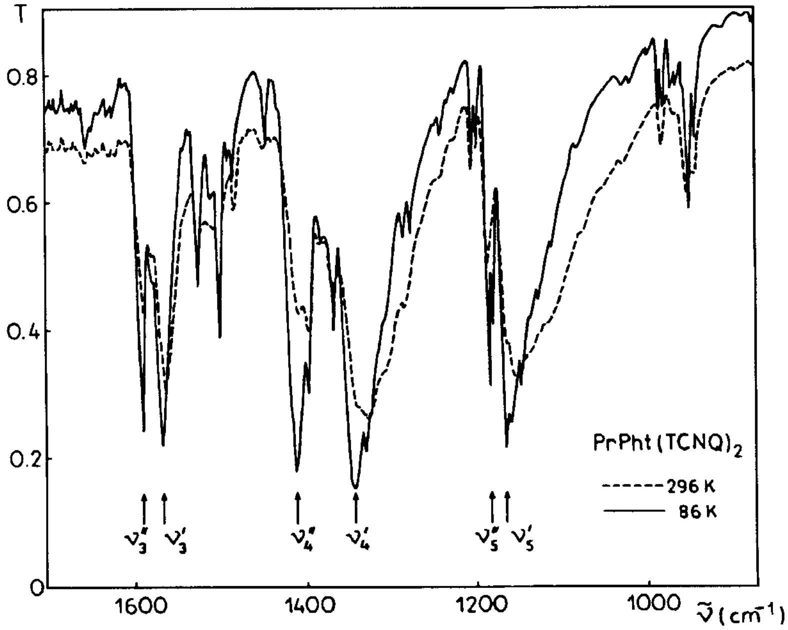

FIGURE 2 Absorption spectra of $PrPht(TCNQ)_2$ powders in KBr pellet for two different temperatures.

perpendicular polarizations are shown in Fig.1 and the absorption spectra of powders in KBr pellet in Fig.2. The bands assigned to a_g modes are split into wide (ν'_α) and narrow (ν''_α) components. The bands ν''_α exhibit stronger temperature dependence in comparison to bands ν'_α

(Fig.2). The spectra of all studied compounds are very similar. The most prominent ν''_α bands are given in Table II. The other a_g bands are also split but the intensity of ν''_α bands is weak, therefore, we do not consider them more thoroughly. On decreasing the temperature from 296 K to 86 K the intensity of ν'_α bands grows about 2 times, whereas the intensity of ν''_α bands grows about 4-6 times.

DISCUSSION

In each studied compound one can distinguish the groups .ABBA. but the degree of isolation of neighbouring tetramers and the organization of molecules inside tetramer are different. In Table I we present transfer integrals calculated[16] from structural data. We notice strong correlation between the degree of tetramer isolation represented by smaller values of t_{AA} and the value of dc conductivity. In TEA $(TCNQ)_2$ at room temperature the interaction between molecules AA is nearly the same as between BB (tetramerization appears at lower temperatures)[8]. In MTPP$(TCNQ)_2$ in the whole temperature range[14,15] and in NPrQn$(TCNQ)_2$ below 220 K [11] the interaction between neighbouring tetramers is weak. From the comparison of bond lengths of TCNQ molecules results that charge is not distributed uniformly between monomers in tetramers. At room temperature average charge density on molecule A equals to about 0.4e and on molecule B about 0.6e.

The most important difference between the spectra of studied salts is connected with the intensity of fine structure. This difference can be correlated with the value of dc conductivity. At room temperature the intensity of ν''_α bands is higher for the salts with lower conductivity. In TEA$(TCNQ)_2$ fine structure is very weak. In NPrQn$(TCNQ)_2$, which exhibits weakly metallic behaviour, the bands ν''_α are not observed in single crystal reflectivity spectra at 300 K (but some small bands were observed in our powder absorption spectra). On the other hand, in MTPP$(TCNQ)_2$, PrPht$(TCNQ)_2$ and PrQuin$(TCNQ)_2$ the bands ν''_α show relatively high intensity at room temperature. The modifications of fine structure due to phase transitions in MTPP$(TCNQ)_2$ at 315.7 K[5] and in NPrQn$(TCNQ)_2$ at 220 K[7] are also in correlation with conductivity.

Yartsev and Rice[17] have attributed the phenomenon of a_g band splitting to a non-uniform charge distiribution. Vibrational frequency depends on the equilibrium molecular charge and the coupling of two oscillators to charge transfer excitation results in an asymmetric doublet in infrared with narrow and relatively weak high frequency ν''_α component. In this approach the splitting of vibronic bands is expected *even* in the case of a *single* electronic charge transfer excitation. Non-uniform equilibrium charge density distribution may be detected by X-ray structural investigation because the bond lengths are related to the molecular charge[18]. Non-uniform charge distribution may be created via asymmetric positions of the counter-ions[19] and/or via organization of trimers, tetramers, etc. inside the molecular stack. The analytical expression for the complex conductivity of tetramerized quasi-one-dimensional compounds including fine structure of vibronic bands is given in Ref. 20. The calculated[20] positions of ν''_α bands for $\alpha = 3$, 4 and 5 in absorption spectrum are given in Table II.

TABLE II

ν_α (cm^{-1})	1602	1454	1207	TCNQ^0 (Ref. 21)
ν_α (cm^{-1})	1615	1391	1196	TCNQ$^-$ (Ref. 21)
ν''_α (cm^{-1})	1596	1412	1198	calculated (Ref. 20)
ν''_α (cm^{-1})	1606	1405	1197	calculated*
ν''_α (cm^{-1})	1578	1400	1183	TEA(TCNQ)$_2$**
ν''_α (cm^{-1})	1585	1403	1183	NPrQn(TCNQ)$_2$**
ν''_α (cm^{-1})	1590	1408	1183	PrPht(TCNQ)$_2$**
ν''_α (cm^{-1})	1585	1400	1183	PrQuin(TCNQ)$_2$**
ν''_α (cm^{-1})	1592	1409	1197	MTPP(TCNQ)$_2$**

*calculated for dimer with two electrons (Ref. 22)
**from powder absorption spectra at room temperature

In the second approach Kaplunov et al.[3] and Świetlik et al.[6] have noticed that ν''_α bands in tetramerized TCNQ salts have the same frequency as the bands in dimerized *simple* TCNQ salts where molecular dimer hosts two radical electrons. Consequently, they have suggested the existence of long living pairs of neighbouring TCNQ$^-$ ions and attributed ν''_α bands as a result of EMV coupling phenomena in $(\mathrm{TCNQ})_2^{2-}$ dimers. In this approach the fine structure is expected *even* in the case of *uniform* charge distribution. We show in Table II the positions of vibronic bands calculated according to this model.

At this stage we can not make a definitive choice between two approaches to explain the fine structure of vibronic bands. The comparison of band positions is not very convincing because vibronic frequencies in crystal could be different up to 10 cm^{-1} (see Ref. 23) from those calculated[21] for isolated molecule. The comparison of band intensities is another possibility which is under investigation in our laboratory.

The work was partially supported by Komitet Badań Naukowych under grant N^{o} 2 0200 91 01.

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