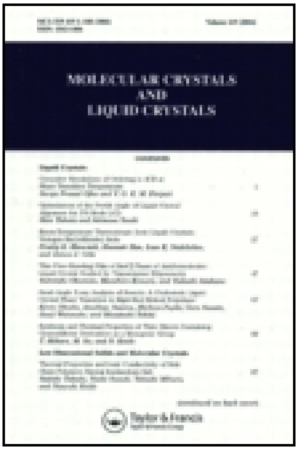

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E. I. Kamitsos [a], G. C. Papavassiliou [a] & M. A. Karakassides [a]

[a] The National Hellenic Research Foundation, Theoretical and Physical Chemistry Institute, Athens, 48 Vas. Constantinou Ave., 116/35, Greece

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ELECTRONIC SPECTRA OF AgTCNQ AND CuTCNQ CHARGE-TRANSFER COMPOUNDS

E.I.KAMITSOS,G.C.PAPAVASSILIOU AND M.A.KARAKASSIDES.
Theoretical and Physical Chemistry Institute, The National Hellenic Research Foundation,48 Vas.Constantinou Ave., Athens 116/35, Greece.

Abstract. The electronic absorption and reflectance properties of CuTCNQ and AgTCNQ have been studied in the visible and near infrared region. AgTCNQ exhibits spectra characteristic of an infinite diadic TCNQ chain, while CuTCNQ shows an additional absorption overlapping with the low energy intramolecular transition. It was observed that the charge transfer band shows a particle size dependence .

INTRODUCTION.

The charge-transfer compounds of tetracyanoquinodimethane (TCNQ)show unusual magnetic, optical and electrical properties. The optical properties are closely related to electrical properties and provide a probe of important interactions in these solids. Based on optical data, Torrance et al. have shown that the critical determinant of the conductivity of TCNQ salts with segregated stacks, is the degree of charge-transfer from donor to TCNQ (1).

CuTCNQ and AgTCNQ have been proven to exhibit electrical switching and phototransformation phenomena (2,3). These are related to the electronic characteristics of the materials. We have studied their optical properties for various sample forms. The results are discussed in connection with structural, magnetic and conductivity data.

EXPERIMENTAL

CuTCNQ and AgTCNQ were prepared by the method of Melby et al (4). Reflectance measurements were performed on pressed pellets. For absorption measurements polycrystalline films were prepared on quartz plates by spraying dilute solutions of the materials in CH_3CN. Homogeneous thin films were prepared by vapor depositing under vacuum alternating layers of metal and TCNQ on quartz plates. The layer structure was heated under vacuum to form M^+TCNQ^-(3).

RESULTS AND DISCUSSION

The CH_3CN solution of CuTCNQ or AgTCNQ give the characteristic spectrum of isolated $TCNQ^-$(Fig.1a). According to theoretical work of Lowitz(5) the red band system (600-900nm) can be assigned to the $^2B_{2g} \rightarrow {}^2B_{1u}^{(1)}$ (long axis polarized) and the blue band system (350-500nm) to overlapping of $^2B_{2g} \rightarrow {}^2B_{1u}^{(2)}$ (long axis polarized) and $^2B_{2g} \rightarrow {}^2A_u$ (short axis polarized) transitions.

Optical studies on various solid TCNQ compounds have been reported by many investigators. The electronic transitions have been grouped by Iida into three types (6). The intramolecular or localized LE_1 and LE_2 transitions correspond to the red and blue band sytems respectively of isolated $TCNQ^-$. These are both polarized in the molecular plane.The intermolecular or charge-transfer (CT) transitions are CT_1 for charge-transfer between two $TCNQ^-$s and CT_2 for charge--transfer from $TCNQ^-$ to $TCNQ^o$. Both CT_1 and CT_2 are polarized in the direction perpendicular to the molecular plane.

Simple 1:1 compounds with complete charge transfer from donor to TCNQ (i.e. LiTCNQ) show the LE_1,LE_2 and CT_1 transitions (6), and their electronic structure is dominated by

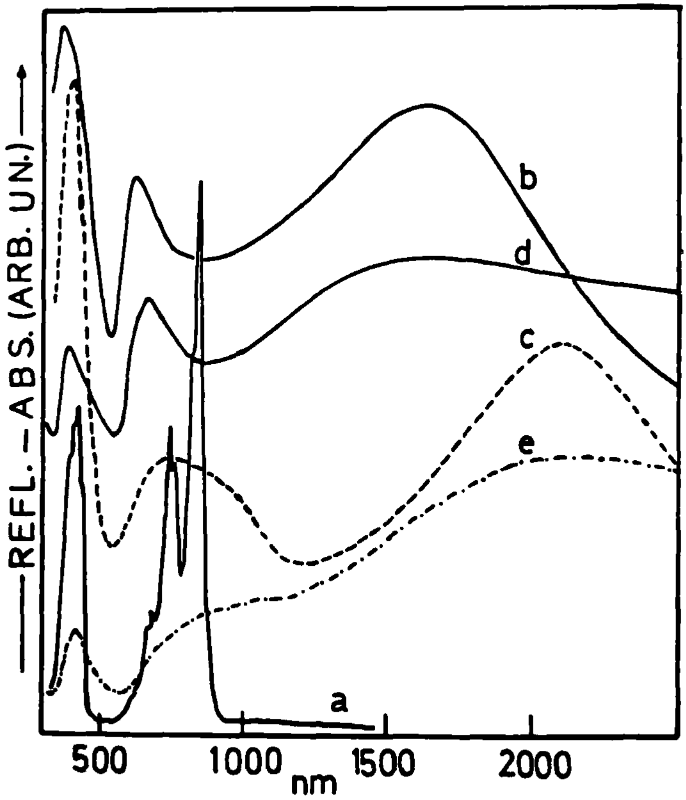

FIGURE 1. Electronic spectra of $TCNQ^-/CH_3CN$ a, AgTCNQ polycrystalline film b, CuTCNQ polycrystalline film c, AgTCNQ reflectance d and **CuTCNQ** reflectance e.

the properties of the dimer type, $(TCNQ)_2^{-2}$ species. This is based on the close resemblance of their solid state optical spectra to that of the dimer type studied by Boyd and Phillips (7). In 1:1 salts with incomplete charge-transfer (i.e. TTF-TCNQ) or in complex 1:2 or 2:3 salts (i.e. $Cs_2(TCNQ)_3$) both CT_1 and CT_2 transitions together with the corresponding LE_1 and LE_2 **localized transitions are observed.**

Both CuTCNQ and AgTCNQ are simple salts with complete charge transfer and thus the LE_1, LE_2 and CT_1 transitions are expected to be exhibited. The absorption spectra of polycrystalline films prepared by the spraying technique are illustrated in Fig.1b and 1c for AgTCNQ and CuTCNQ respectively. To ensure that the nature of the materials is not affected by this method of preparation their reflectance spectra were also measured (Fig.1d,e) from pressed pellets of pure powders of AgTCNQ and CuTCNQ.

The absorption spectrum of AgTCNQ (Fig.1b) shows clearly the LE_1(630nm), LE_2(380nm) and CT_1(1630nm)transitions as expected. The corresponding reflectance spectrum (Fig.1d) is quite similar to the absorption one. The widths of the LE_1 and LE_2 bands are not affected but the CT band appears broader in the reflectance spectrum. A study of the particle size effect on the spectra of KTCNQ and related compounds has shown that CT band shifts to lower frequencies as the size of the particles increases (8). Thus the broadening of the CT band in the reflectance spectrum of AgTCNQ suggests a wide distribution of particle sizes in the pressed pellets of AgTCNQ.

Recently the structure of AgTCNQ was evaluated by lattice imaging using high-resolution electron microscopy(9),and it was found to be similar to those of alkali-TCNQ compounds with $TCNQ^-$ forming diads. An X-ray study of AgTCNQ single crystals was also reported (10). An average interplanar distance of 3.5 A^o was determined; but it is not clear if there is an alternation of the inter-radical spacing. According to Iida for spacing in the range 3.4-3.5 A^o, spectral resemblance to the dimer should be expected (6).Thus we can conclude that AgTCNQ gives spectra typical of a dimer-type TCNQ compound.

The absorption spectrum of CuTCNQ (Fig.1c), while clearly showing the CT_1(2100nm) and LE_2(400nm)bands, differs from that of AgTCNQ in the 650-1000nm region. The LE_1(ca 700nm) band overlaps a broad structure extending to ca 1100nm. This behavior is also exhibited by the reflectance spectrum of CuTCNQ (Fig.1e), and it was observed in the spectrum of CuTCNQ thin film as well (11).

The crystal structure of CuTCNQ is unfortunately not known yet, thus it would be difficult to give an exact interpretation of the additional broad band of the spectrum of CuTCNQ. A similar situation was observed in the spectrum of solid LiTCNQ which also exhibits an extra band at 840nm. The origin of this peak was attributed to non-dimerized $TCNQ^-$, due to imperfections in the alternation of the $TCNQ^-$ separations (6,12). The so called impurity resonance observed in the ESR spectrum of LiTCNQ was also associated with the presence of unpaired $TCNQ^-$(13). A similar impurity resonance was found in the ESR spectrum of CuTCNQ powder and that would also suggest the presence of non-dimerized $TCNQ^-$.This would give rise to a peak at ca 840nm in the optical spectrum by comparison to the LiTCNQ case. However, the additional absorption structure of CuTCNQ is much broader than is accounted for only by the presence of non-dimerized $TCNQ^-$, since an obvious shoulder in the 980-1000nm region is involved as well.

Recent results from ESR studies on CuTCNQ single crystal suggested that the narrow-band structure of TCNQ is modified by coupling to copper 3d bands (10). This coupling involves hole formation in the 3d band of copper and an equal amount of $TCNQ^=$ formation. A similar conclusion was also reached from Seebeck coefficient values of CuTCNQ (12). In light of the above discussion we tentatively assign the ca 980nm shoulder to charge-transfer from the full d orbitals of Cu^+ to the low lying empty molecular orbitals of $TCNQ^-$.

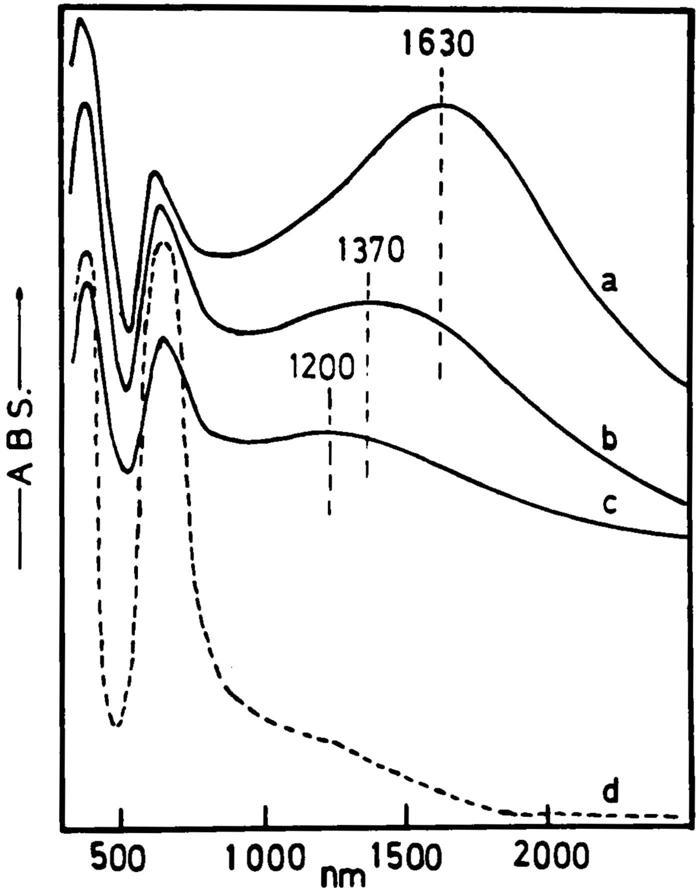

FIGURE 2. Particle size effect on absorption spectra of AgTCNQ; a: as prepared polycrystalline film; b,c:after succesive rubbing with soft tissue paper; d:AgTCNQ thin film.

Polarized optical measurements on single crystals of CuTCNQ are required to give a conclusive assignment (15).

Figure 2 illustrates the effect of particle size on the absorption spectrum of AgTCNQ. Succesive rubbing, and presumably formation of smaller particles, causes a systematic shift of the CT band to higher energies, upon reduction of its intensity. The two intramolecular bands are almost unaffected by particle size. The spectrum of the thin film shows the CT band as a shoulder at ca 1150nm, and it very much resembles a spectrum of the dimer type (7).Particle size dependence has been reported for KTCNQ (8) and other semiconductor materials (16). This dependence has been interpreted as essentially a quantum size effect (8,16).

The particle size effect for CuTCNQ is shown in Fig.3. The CT band behaves in the same way as that for AgTCNQ. In addition decrease of particle size causes a systematic increase in the intensity of the absorption attributed to transitions of $TCNQ^-$ monomer and charge-transfer from Cu^+ to $TCNQ^-$. This could be understood by the fact that rubbing also causes defect formation and thus an increase in the number of non-dimerized $TCNQ^-$ monomers.

It is interesting to note that CuTCNQ has the highest conductivity ($1\times10^{-2}\Omega^{-1}cm^{-1}$) among the known simple 1:1 anion-radical TCNQ compounds with complete charge transfer (4,17),and the lowest energy CT band. This appears at 2100 nm in the absorption spectrum of polycrystalline film. For intrinsic semiconductors the activation energy for conduction (E) is related to the gap energy (Eg) for hole-electron pair formation by $E=Eg/2$ (18). Activation energies for conduction, obtained from powder conductivity data, are 0.16eV for CuTCNQ and 0.37 eV for AgTCNQ (17). The optical gap energies estimated from the reflectance spectra are about 0.55eV for CuTCNQ and 0.75 eV for AgTCNO, and the corresponding activation energies obtained from the above values are 0.27 eV for CuTCNQ and 0.38 eV for AgTCNQ. Comparison shows a quite good agreement with the experimental activation

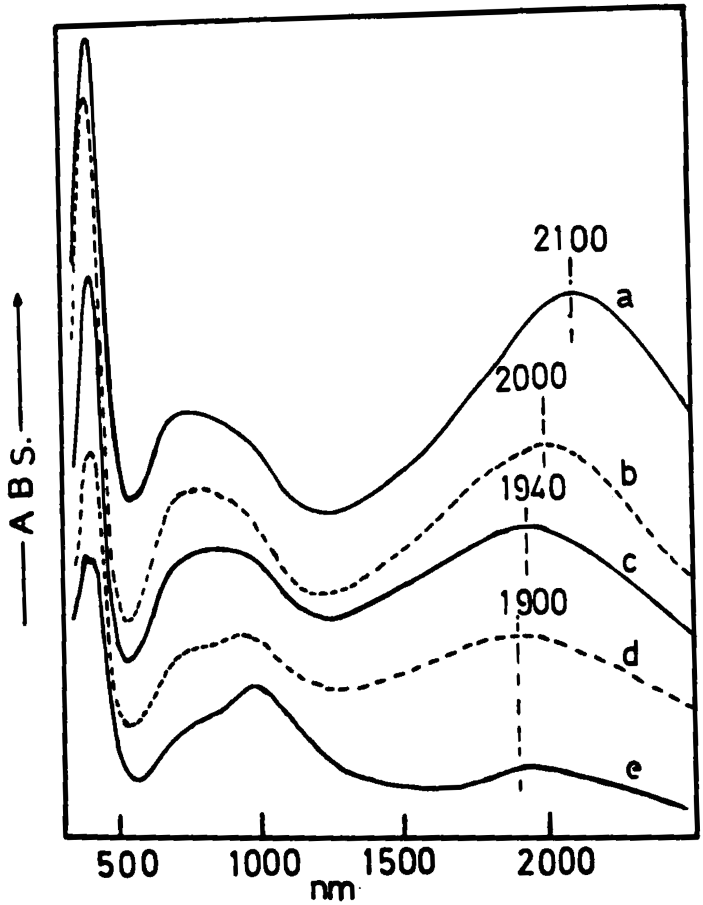

FIGURE 3. Particle size effect on the absorption spectra of CuTCNQ; a: as prepared polycrystalline film;b,c,d,e: after succesive rubbing with soft tissue paper.

energies for conduction indicating the close correspondance between the conductivity and the optical data.

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