which does not necessarily[10] correspond to the minimum magnetic field point.

It is a pleasure to thank G. Rewoldt for his very valuable comments and corrections.

---

*Work supported in part by the U.S. Atomic Energy Commission under Contract No. AT(11-1)-3070.

[1] G. A. Bobrovskii, E. I. Kutznetsov, and K. A. Razumova, Zh. Eksp. Teor. Fiz. 59, 1103 (1970) [Sov. Phys. JETP 32, 599 (1971)].

[2] B. Coppi and E. Mazzucato, Phys. Fluids 14, 134 (1971).

[3] B. B. Kadomtsev and O. P. Pogutze, Zh. Eksp. Teor. Fiz. 53, 2025 (1967) [Sov. Phys. JETP 26, 1146 (1968)].

[4] L. I. Rudakov, in *Plasma Physics and Controlled Thermonuclear Research 1971* (International Atomic Energy Agency, Vienna, Austria, 1971), Vol. II, p. 235.

[5] A. Bers, B. Coppi, T. Dupree, F. Santini, and R. Kulsrud, in *Plasma Physics and Controlled Thermonuclear Research 1971* (International Atomic Energy Agency, Vienna, Austria, 1971), Vol. II, p. 247.

[6] B. Coppi and F. Santini, Phys. Rev. Lett. 28, 1 (1972).

[7] B. Coppi and R. Pozzoli, Massachusetts Institute of Technology R.L.E. Report No. PRR-732, 1973 (to be published).

[8] D. W. A. Withfield, Plasma Physics Laboratory, University of Saskatchewan, Report No. PLL-33, 1971 (unpublished).

[9] A. Hirose, S. Q. Ma, H. M. Skargaard, A. R. Strilchuk, and D. W. A. Whitfield, Phys. Rev. Lett. 28, 1185 (1972).

[10] H. M. Skargaard, private communication.

---

# Valence Electronic Structure and Charge Transfer in Tetrathiofulvalinium Tetracyanoquinodimethane (TTF-TCNQ) from Photoemission Spectroscopy

W. D. Grobman, R. A. Pollak, D. E. Eastman, E. T. Maas, Jr., and B. A. Scott
*IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598*

(Received 26 December 1973)

Comparison of ultraviolet-photoemission, valence-orbital spectra (as well as high-resolution, x-ray photoemission, N-core–level spectra) of TTF-TCNQ, neutral TCNQ, and $K^+(TCNQ)^-$ indicates a large amount of charge transfer in TTF-TCNQ. The spectra for this complex show strong coupling between states near the Fermi energy and molecular vibrations due to localization of the mobile electrons on individual molecules, at least on the time scale of bond vibrations.

Recent interest in conducting organic complexes of tetracyanoquinodimethane (TCNQ) has been stimulated by reports[1,2] of large conductivity peaks [typically $\sim 10^4$ $(\Omega\ \mathrm{cm})^{-1}$ at $\sim 60$ K] in the tetrathiofulvalinium (TTF) complex of TCNQ. Several questions of importance for understanding the transport,[1-3] optical,[4,5] and magnetic[6,7] studies of TTF-TCNQ are the following: (a) What is the nature of the conducting states (localized versus extended)? (b) How much charge is transferred from TTF to TCNQ upon formation of the complex? (c) What is the valence-orbital electronic structure of these materials?

Considering the nature of the conducting states, the valence-electron spectra of TTF-TCNQ show that the states near $E_\mathrm{F}$ are localized in orbitals confined to individual molecules, at least on the time scale of bond vibrations. Such short-time localization could be simply a consequence of the narrow bandwidth ($h$/bandwidth $\approx$ bond vibration period). Concerning charge transfer, consideration of the valence-band and N-1$s$ core-level spectra suggests that $(TTF)^+$ and $(TCNQ)^-$ are the charge states of a majority ($\gtrsim \frac{2}{3}$) of the cation and anion molecules in TTF-TCNQ at 300 K.

Ultraviolet-photoemission (UPS) spectra were obtained using a previously described[8] spectrometer with a typical electron energy resolution of $\sim 0.25$ eV. Samples [except for $K^+(TCNQ)^-$][9] were sublimed *in situ* in the measurement chamber from an effusion oven onto a Au-coated quartz substrate which served both as a calibration sample to determine the Fermi-level position, $E_\mathrm{F}$, and as an electrical contact to the sample film. Pressure in the sample vicinity was typically $\sim 1\times10^{-6}$ Torr, dominated by the vapor pressure of the sample. The partial pressure of the background gas in the (unbaked) chamber was $\sim 5\times10^{-8}$ to $1\times10^{-7}$ Torr. The possibility of sample contamination effects was excluded by obtaining spectra simultaneous with film deposition. Other measurements made on films which were several hours old gave spectra almost identical to those obtained during continuous film deposition, perhaps due to self-cleaning of the surface by its continual slow sublimation at room temperature.

After UPS measurements on these films, their structure and composition was checked by x-ray diffraction and, in some cases, by infrared absorption and scanning electron microscopy of the film. An additional check in the case of TTF-TCNQ was the verification that x-ray photoemission (XPS) valence orbital spectra were the same for samples in evaporated film form as for those in the form of solution-grown crystals.

XPS spectra were obtained[10,11] in a Hewlett-Packard model 5950A spectrometer which uses a photon energy of $h\nu = 1486.6$ eV and typically achieves ~0.6-eV electron energy resolution. Samples for XPS studies were prepared in a separate vacuum system and transferred to the XPS system in an inert atmosphere. Samples studied using this technique included films of TCNQ, TTF-TCNQ, and $K^+(TCNQ)^-$, as well as a compressed pellet of solution-grown TTF-TCNQ crystallites. In all cases the XPS valence orbital spectra agreed with the UPS spectra.

UPS spectra at $h\nu = 21.2$ eV for neutral TTF and for neutral TCNQ are shown as unbroken lines in Figs. 1(a) and 1(b), respectively, where we have plotted the emission intensity versus the initial energy of the photoelectron (the negative of its ionization potential) relative to $E_F \equiv 0$. In Fig. 1(a) we also show (dashed line) the spectrum of vapor-phase TTF obtained by Gleiter *et al.*[12] Their energy scale (ionization potential referred to the vacuum level) has been placed so that features in the two spectra coincide. The relative energy levels in solid and vapor-phase TTF are in excellent agreement. This implies that the intramolecular electronic structure remains dominant and is relatively unperturbed by condensation into the solid. Comparison of spectra for solid and vapor-phase TTF indicates that the width of the emission feature corresponding to a given initial orbital in the solid appears to be determined in part by the Franck-Condon effect.[13] That is, during the emission process from an orbital with a well-defined initial energy, various molecular vibrations of the ionized molecule left behind are excited, leading to a range of energies of the emitted electron corresponding to the width of the observed emission feature for the gas-phase molecule. Comparing the least-bound orbital widths in solid and vapor phase TTF in Fig. 1(a), we see an additional solid-state broadening of about 0.5 eV. Also, comparison of the energy scales of the TTF spectra in Fig. 1(a) yields a solid-state shift of all orbital energies of +0.4 eV relative to the gas phase.[14]

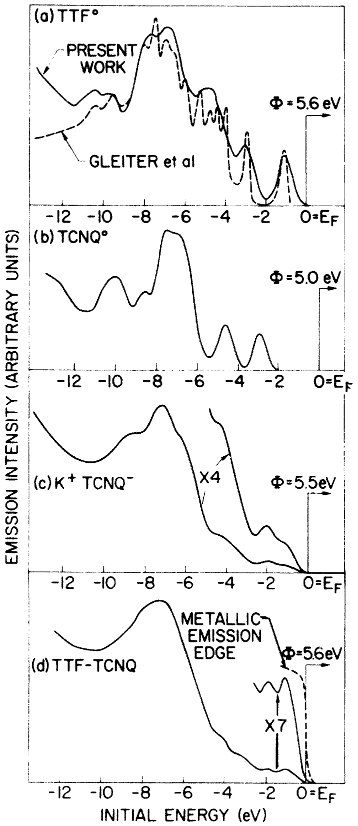

FIG. 1. In these UPS spectra ($h\nu = 21.2$ eV), emission intensity (arbitrary units) is plotted versus the initial energy $E_i$ of the emitted photoelectrons, measured with respect to the Fermi energy $E_F$. Spectra are plotted with a common vacuum level, and the work function is given for each material (uncertain to within ~0.25 eV). $E_F$ is uncertain to ~0.1 eV for (c) and (d), while this uncertainty is ~0.25 eV for 1(a) and 1(b) because of sample charging.

In the TTF emission spectrum there are two distinct, well separated, high-lying orbitals, with emission centered at initial energies of ~ −1.0 and −3.0 eV, as well as a series of lower-lying orbitals, many of them superimposed. Similarly, pure TCNQ contains two distinct high-lying orbitals with emission peaks centered at initial energies of −2.9 and −4.6 eV as well as many lower-lying orbitals at energies $-11 \lesssim E_i \lesssim -6$ eV.

Figure 1(c) displays the $K^+(TCNQ)^-$ spectrum. This spectrum consists of three high-lying spectral features bound at ~ −1.0, −2.0, and −4.2 eV, as well as more intense emission between ~ −6 and −12 eV. Since $K^+$ has no valence electrons, this spectrum essentially represents that of $(TCNQ)^-$. The emission features at −2.0 and

$-4.2$ eV most likely correspond to the two high-lying $\pi$-orbitals seen at $-2.9$ and $-4.6$ in neutral TCNQ, while the feature at $-1.0$ eV corresponds to the singly occupied affinity level. The emission features below $\sim -6$ eV in neutral TCNQ and in $(\text{TCNQ})^-$ are dissimilar in spectral shape. One possible explanation is that in $(\text{TCNQ})^-$ the presence of the unpaired affinity-level electron exchange splits some of the lower-lying orbitals enough to cause the observed loss of sharp structure. Also, we see a gap ($\sim 0.3$ eV wide) between $E_F$ and the upper edge of the valence-band spectrum, consistent with the fact that $K^+(\text{TCNQ})^-$ is a semiconductor.

Consider now the emission spectrum from TTF-TCNQ shown in Fig. 1(d). For this complex, there are four distinct high-lying orbitals, at initial energies $E_i$ of $\sim -1.0$, $-1.9$, $-3.0$, and $-4.1$ eV, as well as more intense emission for $-9 \text{ eV} \lesssim E_i \lesssim -5$ eV. The emission intensity of the highest-lying spectral feature falls smoothly to a very small value at $E_F$ from the peak at $-1.0$ eV, in contrast to the spectral shape of a typical metallic band at $E_F$ [such as that for Au shown in Fig. 1(d)] which shows significant emission near $E_F$, cut off at $E_F$ by the Fermi function broadened by the ($\sim 0.25$-eV) instrumental resolution. Thus it appears that the electrons near $E_F$ are in localized molecular orbital states, e.g., $\pi$ orbitals, confined to individual molecules.[15] Such states are strongly coupled to molecular vibrations in the photoionization process (Franck-Condon effect[16]) and thus produce emission which is broadened and shifted to lower energies. The rather narrow bandwidth in this material[4] may be comparable to energies corresponding to typical bond vibrations ($\sim 0.2$ eV). Thus short-time-scale localization of electrons as a result of the narrow bandwidth might explain our observations.

The question arises of whether metallic emission is absent because the short photoemission escape depth causes us to measure surface molecular layers that are not characteristic of the bulk. This does not seem to be the case for several reasons. Namely, spectra obtained with an 11.7-eV photon energy show the same orbital structure as do 21.2-eV spectra, although the photoelectron escape depth is probably 2 to 3 times as great at 11.7 eV. In addition, the XPS valence spectrum in Fig. 2(a) (inset) shows the same orbitals near $E_F$ as are seen in the UPS spectrum in Fig. 1(d), although the XPS spectrum samples significantly deeper into the solid.[16]

The spectra in Figs. 1(a)-1(c) are now compared with that of TTF-TCNQ [Fig. 1(d)] in order to consider the question of charge transfer. We assume that intramolecular energies dominate so that the spectrum of the complex is essentially a superposition of the spectra of the constituents, in the appropriate charge states. Upon performing such a comparison, we see that the three highest-lying orbitals of $K^+(\text{TCNQ})^-$ in Fig. 1(c) are bound at the same positions (within experimental error) as three of the four highest-lying orbitals in TTF-TCNQ, namely, those at $-1.0$, $-1.9$, and $-4.1$ eV. This excellent agreement between orbital positions strongly suggests a preponderance of $(\text{TCNQ})^-$ over neutral TCNQ in TTF-TCNQ. In such a case the TTF-TCNQ orbitals at $-3.0$ eV, as well as part of the emission intensity at $-1.0$ eV, could be due partly to neutral TTF which has levels at $-1.0$ and $-3.0$ eV, as well as to the upper two orbitals of $(\text{TTF})^+$, whose energies have not yet been determined experimentally, but which are derived from the $-1.0$ and $-3.0$ orbitals of neutral TTF.

In Fig. 1 we have placed the energy scales of the various spectra so that their vacuum levels are at a common energy. Using this reference energy we find that the two highest-lying orbitals of neutral TTF and the two highest-lying orbitals of neutral TCNQ lie at positions close (within $\sim 0.3$ eV) to those of the four highest-lying orbitals of TTF-TCNQ. For this reason emission from a small amount of neutral TTF and TCNQ could be present in the TTF-TCNQ spectrum. However, the unusually good agreement between the positions of the $(\text{TCNQ})^-$ orbitals and those of TTF-TCNQ, as well as the spectral shape of the emission below $-6$ eV, indicates that most[17] of the emission (probably $\gtrsim \frac{2}{3}$) is due to $(\text{TTF})^+$ and $(\text{TCNQ})^-$.

Support for such a model also comes from the XPS N-1*s* core-level spectra shown in Fig. 2(b). In the cases of TCNQ and $K^+(\text{TCNQ})^-$ we see a single main N-1*s* core-level peak and a weaker satellite with higher binding energy. In the case of TTF-TCNQ there are at least two main N-1*s* peaks as well as the weaker satellite structure. Considering the multiple main peaks in TTF-TCNQ to represent *chemical states* of N in TCNQ, the N-1*s* spectrum is consistent with both neutral TCNQ and $(\text{TCNQ})^-$ molecules in the solid, with $(\text{TCNQ})^-$ dominating.[18] For this reason both the core and valence-band spectra independently confirm the presence of mostly charged species in TTF-TCNQ, and consequently significant filling of any bands formed from their high-lying molec-

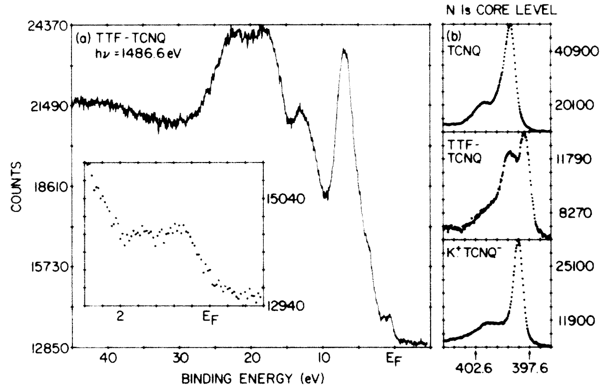

FIG. 2. (a) The x-ray photoemission spectrum ($h\nu = 1486.6$ eV) of the TTF-TCNQ valence bands (~ 35 eV wide) and of the highest-lying orbitals (inset). $E_F$ is determined to ~ ± 0.1 eV. (b) N-1$s$ core-level spectra for neutral TCNQ, TTF-TCNQ, and $K^+(TCNQ)^-$.

ular orbitals.

We acknowledge useful conservations with A. Bloch, A. Heeger, J. J. Hopfield, Y. Tomkiewicz, and J. B. Torrance, and the technical assistance of R. C. Braccini and G. J. Padilla. We are grateful to D. C. Green for supplying us with samples of TTF.

---

[1] J. P. Ferraris, D. O. Cowan, V. V. Walatka, and J. H. Perlstein, J. Amer. Chem. Soc. 95, 948 (1973).

[2] L. B. Coleman, M. J. Cohen, D. Sandman, F. G. Yamagishi, A. F. Garito, and A. J. Heeger, Solid State Commun. 12, 1125 (1973).

[3] P. M. Chaikin, J. F. Kwak, T. E. Jones, A. F. Garito, and A. J. Heeger, Phys. Rev. Lett. 31, 601 (1973).

[4] A. A. Bright, A. F. Garito, and A. J. Heeger, Solid State Commun. 13, 943 (1973); P. M. Grant, R. L. Greene, G. C. Wrighton, and G. Castro, Phys. Rev. Lett. 31, 1311 (1973).

[5] J. B. Torrance *et al.*, to be published.

[6] J. Perlstein, J. P. Ferraris, V. V. Walatka, D. O. Cowan, and G. G. Candela, in *Magnetism and Magnetic Materials—1972*, AIP Conference Proceedings No. 10, edited by C. D. Graham, Jr., and J. J. Rhyne (American Institute of Physics, New York, 1973).

[7] Y. Tomkiewicz, F. Mehran, L. J. Tao, R. S. Title, and B. A. Scott, "Magnetic Properties of TTF-TCNQ" (to be published).

[8] J. K. Cashion, J. L. Mees, D. E. Eastman, J. A. Simpson, and C. E. Kuyatt, Rev. Sci. Instrum. 42, 1670 (1971).

[9] Samples of $K^+(TCNQ)^-$ were in the form of films on Au substrates, prepared by direct reaction of vapors of TCNQ and K in an evacuated, sealed glass tube (E. T. Maas, Jr., to be published), and cleaned by scraping *in situ* in the evacuated sample chamber.

[10] Previously, low-resolution (~ 1.5 eV) XPS core-level spectra have been presented for some TCNQ salts. See I. Ikemoto, J. M. Thomas, and H. Kuroda, Faraday Discuss. Chem. Soc. 54, 208 (1972), and L. J. Aarons et al., J. Chem. Soc., Faraday Trans. II 69, 270 (1973).

[11] M. A. Butler, J. P. Ferraris, A. N. Bloch, and D. O. Cowan (to be published) use x-ray photoemission spectra (resolution ~ 1.5 eV) of the S-2$p$ core levels in TTF-TCNQ to support the argument for large charge transfer. However, we see from our higher resolution S-core-level spectra that there are multiple chemical states of S not seen by them. For this reason their analysis of the amount of charge transfer, based on the assumption that their spectrum arises from a *single* spin-orbit split level, is suspect.

[12] R. Gleiter, E. Schmidt, D. O. Cowan, and J. P. Ferraris, J. Electron. Spectrosc. 2, 207 (1973).

[13] See D. W. Turner *et al.*, *Molecular Photoelectron Spectroscopy* (Wiley, London, 1970), Chap. 1.

[14] Such a positive shift is seen in other organic solids, e.g., in K. Seki, H. Inokuchi, and Y. Harada, Chem. Phys. Lett. 20, 197 (1973).

[15] If the conduction electrons were simply in uncorrelated, nonlocalized states (simple-metal limit), a Fermi edge would have been evident in Fig. 1(d). More quantitatively, we would easily detect such an edge if the density of metallic electrons near $E_F$ were ~ 0.4 electrons/eV (e.g., 0.1 electron in an 0.5-eV total width band, or 1 electron in an ~ 5-eV-wide one-dimensional band).

[16] Note that the XPS spectrum, because of the high photon energy used, displays the entire valence-band structure (~ 35 eV wide). Also, the UPS spectrum emphasizes high-lying $\pi$-like orbitals relative to $\sigma$ orbitals, compared with the XPS spectrum. This causes different spectral shapes for the two spectra. However, corresponding emission features are at the same binding energies in the two spectra within the combined experimental error (~ 0.2 eV), as we have stated. In particular, the structure near $E_F$, shown in the inset in Fig. 2, is identical to that seen in the UPS spectrum in Fig. 1(d).

[17] Several authors have discussed the possibility of significant but not total charge transfer. For example see Y. Tomkiewicz, J. B. Torrance, B. A. Scott, and D. C. Green, "Charge Transfer Equilibria in TTF-TCNQ Solutions" (to be published), and references therein. Also, see Ref. 11.

[18] Alternatively, a portion of the new, multiple-peak structure in TTF-TCNQ could be associated with new photoexcitation-loss processes occurring as a result of the proximity of TTF and TCNQ molecules, However this latter possibility is at present speculative.