PHYSICAL REVIEW B VOLUME 11, NUMBER 12 15 JUNE 1975

Simple molecular model for crystalline tetrathiofulvalene-tetracyanoquinodimethane (TTF-TCNQ)

I. P. Batra, B. I. Bennett, and Frank Herman
IBM Research Laboratory, San Jose, California 95193

(Received 12 August 1974; revised manuscript received 17 March 1975)

The energy-level structure of solid tetrathiofulvalene-tetracyanoquinodimethane(TTF-TCNQ) is approximated by superimposing the energy levels of the radical ions TTF^+ and $TCNQ^-$. The energy levels for these ions were obtained by carrying out self-consistent statistical-exchange multiple-scattering calculations using overlapping-atomic-sphere molecular models. It is possible to account for many of the principal features of the experimental photoemission spectrum of solid TTF-TCNQ by shifting the free cation TTF^+ and the free anion $TCNQ^-$ energy levels upwards and downwards by 3.8 eV, respectively. These features can also be accounted for by assuming less than unity charge transfer and shifting the constituent-ion energy levels by proportionally smaller amounts. The next to the highest experimental photoemission peak cannot be reproduced by energy level models of the type just described. We propose that this peak is due to electronic transitions from neutral TCNQ or neutral TTF molecules lying on the surface immediately above TTF^+ or $TCNQ^-$ ions, respectively.

INTRODUCTION

An active area of research in physics today is the study of highly conducting organic solids such as tetrathiofulvalene-tetracyanoquinodimethane (TTF-TCNQ).[1] Their near one-dimensional character leads to new, exciting, and puzzling electronic phenomena. We have recently calculated the electronic structure of isolated neutral TCNQ[2,3] (tetracyanoquinodimethane—$C_{12}N_4H_4$) and TTF[4] (tetrathiofulvalene-$C_6S_4H_4$) molecules using the overlapping-atomic-sphere version[5,6] of the self-consistent statistical-exchange multiple-scattering method.[7–9] Since the theoretical models obtained for $TCNQ^0$ and TTF^0 were able to account for the experimental photoemission spectra of TCNQ and TTF vapor, and of solid TCNQ and TTF, we decided to determine the electronic structure of the radical ions $TCNQ^-$ and TTF^+ and attempt to interpret some of the features of the experimental photoemission spectra for TTF-TCNQ.[10]

After briefly reviewing our earlier results for $TCNQ^0$ and TTF^0, we will report our new results for $TCNQ^-$ and TTF^+. We will then construct a family of simplified energy-level models for the TTF-TCNQ crystal based on these results. At one extreme we will assume that the energy-level structure of crystalline TTF-TCNQ can be approximated by superimposing the energy-level structures of isolated TTF^0 and $TCNQ^0$ molecules; at the other extreme, of isolated TTF^+ and $TCNQ^-$ molecules. We will also consider intermediate cases involving charge transfer between zero and unity. In all cases we will not attempt to calculate polarization effects or Madelung shifts. Rather, we will simulate these effects by rigidly shifting the energy levels of the constituent molecules (TTF^{+x}, $TCNQ^{-x}$, $0<x\leq 1$) by the amounts necessary to bring the highest partially occupied energy level of TTF^{+x} into registry with the lowest partially unoccupied energy level of $TCNQ^{-x}$. For the purposes at hand, we neglect the k dependence of the valence and conduction bands, and assume that all bands in the neighborhood of the Fermi level have zero width. The k dependence of the bands, which is of considerable importance in understanding the electronic transport properties of solid TTF-TCNQ, is currently being investigated on the basis of our molecular models.

It can be seen that we are primarily interested here in the gross features of the energy-level structure of solid TTF-TCNQ, rather than in the details (e.g., k dependence). In attempting to map out these gross features, we will take advantage of the physical realism that we believe we have achieved in determining the electronic structure of the molecular constituents of solid TTF-TCNQ. As an immediate application of our present work, we will interpret the photoemission spectrum of solid TTF-TCNQ in terms of our energy-level scheme.

II. MOLECULAR-STRUCTURE CALCULATIONS FOR TTF^0, TTF^+, $TCNQ^0$, AND $TCNQ^-$

It is sufficient for our purposes to describe the calculations for all these molecules in abbreviated form. More extensive discussions appear in Refs. 2, 3, 4, and 6. The calculations are based on molecular models in which the various atoms are represented by overlapping atomic spheres. The geometrical models used for TTF^0 and TTF^+ are shown in Fig. 1 and those for $TCNQ^0$ and $TCNQ^-$ in Fig. 2. For each molecule, the set of atomic spheres is surrounded by a circumscribing outer sphere (OUT 1). The outer sphere is always taken to be externally tangent to the outermost atomic spheres.

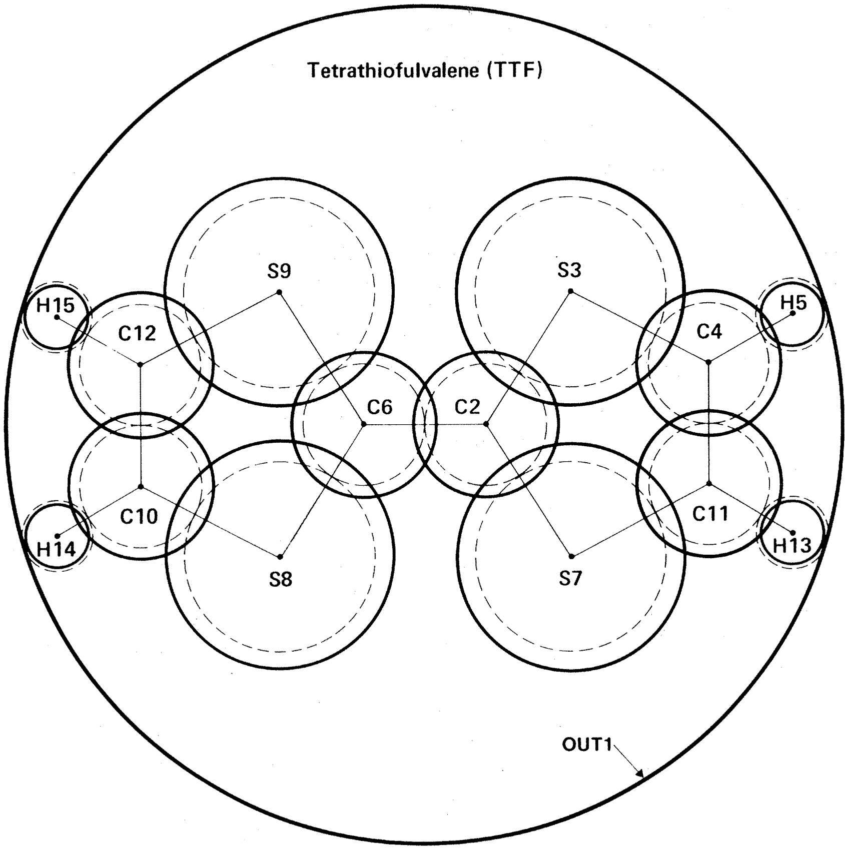

FIG. 1. Nonoverlapping-atomic-sphere model (dashed circles) and overlapping-atomic-sphere model (solid circles) for TTF and TTF^+ molecules. The molecule lies in the x-y plane, with the x and y axis pointing along the long and short axis of the molecule, respectively. The outer sphere (OUT 1) is assigned serial number 1 and the atomic spheres serial numbers 2 through 15. The molecule is assumed to have D_{2h} symmetry. (See Table I for detailed molecular geometry).

Charge distributions and potentials are spherically averaged within each atomic sphere and outside the outer sphere, and volume averaged in the intersphere region. The theoretical basis for the overlapping-atomic-sphere version of the self-consistent statistical-exchange multiple-scattering method has been discussed earlier.[6]

All our molecular-structure calculations were carried out self-consistently using a statistical-exchange parameter $\alpha = 0.75$. Spherical harmonics up to $l_{\max} = 4$ and 2 were employed outside the bounding sphere and inside the atomic spheres, respectively. The atomic sphere radii were determined on the basis of various theoretical and empirical considerations (cf. Refs. 2, 3, 4, 6). The atomic dimensions for TTF^0 and TCNQ^0 were obtained from x-ray crystallographic data from crystalline TTF[11] and crystalline TCNQ.[12] Although it is known[11] that the atomic dimensions of TTF^+ and TCNQ^- are slightly different from those for TTF^0 and TCNQ^0, we decided to ignore these differences and use the same atomic dimensions for TTF^+ and TCNQ^- that we used earlier for TTF^0 and TCNQ^0. Considering the simplicity of our theoretical model, it seemed to be an unnecessary refinement to take these small differences into account. In all cases (TTF^0, TTF^+, TCNQ^0, TCNQ^-) the molecule was assumed to be planar and to have D_{2h} symmetry. Molecular geometry used in computing TTF is given in Table I, and for TCNQ in Table II. We will use the symmetry notation of Cotton[13] for the D_{2h} point group. In

TABLE I. Molecular geometry for the TTF° (and TTF^+) molecule.[a]

Center[b]	x	y	Sphere radius
OUT 1	0.000	0.000	8.717
C 2	1.294	0.000	1.561
S 3	3.070	2.774	2.396
C 4	5.975	1.250	1.561
H 5	7.738	2.314	0.641
C 6	−1.294	0.000	1.561
S 7	3.070	−2.774	2.396
S 8	−3.070	−2.774	2.396
S 9	−3.070	2.774	2.396
C 10	−5.975	−1.250	1.561
C 11	5.975	−1.250	1.561
C 12	−5.975	1.250	1.561
H 13	7.738	−2.314	0.641
H 14	−7.738	−2.314	0.641
H 15	−7.738	2.314	0.641

[a] All values are given in atomic units; the value of the z coordinate is zero.

[b] See Fig. 1 for labels for various centers.

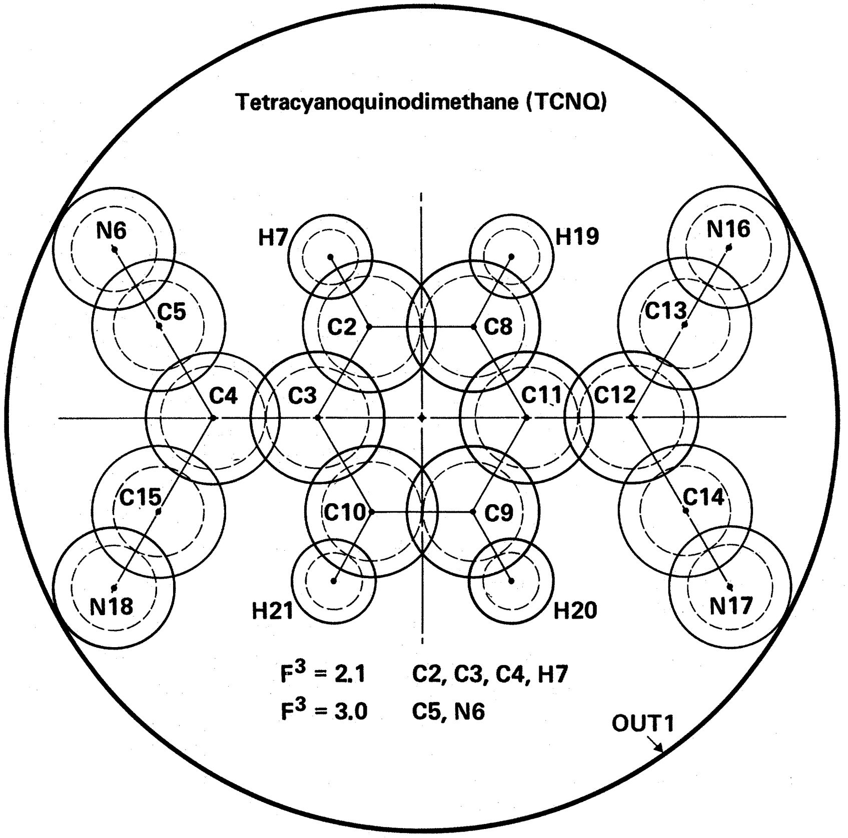

FIG. 2. Nonoverlapping-atomic-sphere model (dashed circles) and overlapping-atomic-sphere model (solid circles) for the TCNQ and TCNQ$^-$ molecules. The outer sphere (OUT 1) for the former is not shown in the interest of clarity. The outer sphere is assigned serial number 1 and the atomic spheres serial numbers 2 through 21. The ratio of the volumes of the overlapping and corresponding nonoverlapping atomic spheres is denoted by F^3. (See Table II for detailed molecular geometry).

all four cases we will report results based on spin-restricted calculations.

III. ENERGY-LEVEL STRUCTURE OF TCNQ^0 AND TTF^0

The energy-level structures obtained earlier[2,4] for TCNQ^0 and TTF^0 are shown together for reference in Fig. 3 and are listed in Tables III and IV for completeness. All the energy levels were obtained by the transition-state method[7,14] so that electronic relaxation effects are taken into account. Occupied levels are denoted by solid lines, unoccupied levels by dashed lines.

Let us briefly explain how the unoccupied energy levels are obtained, what their physical significance is, and how the relaxation effects are built into the calculation. The ionization energy for level *A* is given by the energy eigenvalue of the self-consistent solution for which level *A* is occupied by 1.5 electrons, and all other (occupied) levels by 2 electrons. In order to determine the excitation energy corresponding to a transition from the initially full level *A* to the initially empty level *B*, one takes the difference in the energy eigenvalues of *A* and *B* for the self-consistent solution for which level *A* contains 1.5 electrons, level *B* contains 0.5 electron,

TABLE II. Molecular geometry for the TCNQ^0 (and TCNQ$^-$) molecule.[a]

Center[b]	*x*	*y*	Sphere radius
OUT 1	0.000	0.000	10.384
C 2	−1.272	2.346	1.629
C 3	−2.681	0.000	1.663
C 4	−5.278	0.000	1.663
C 5	−6.721	2.309	1.607
N 6	−7.862	4.136	1.500
H 7	−2.302	4.129	1.009
C 8	1.272	2.346	1.629
C 9	1.272	−2.346	1.629
C 10	−1.272	−2.346	1.629
C 11	2.681	0.000	1.663
C 12	5.278	0.000	1.663
C 13	6.721	2.309	1.607
C 14	6.721	−2.309	1.607
C 15	−6.721	−2.309	1.607
N 16	7.862	4.136	1.500
N 17	7.862	−4.136	1.500
N 18	−7.862	−4.136	1.500
H 19	2.302	4.129	1.009
H 20	2.302	−4.129	1.009
H 21	−2.302	−4.129	1.009

[a] All values are given in atomic units; the value of the *z* coordinate is zero.

[b] See Fig. 2 for labels for various centers.

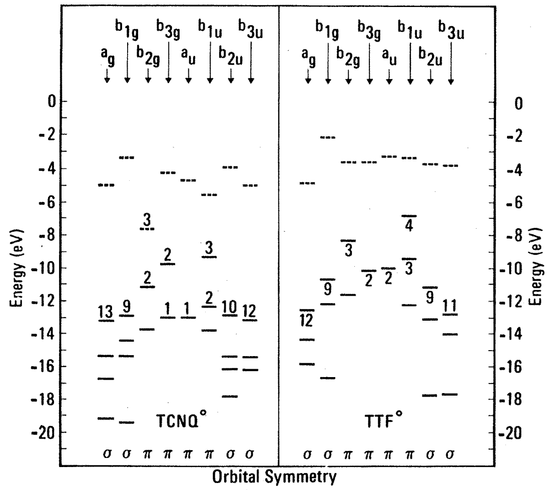

FIG. 3. Calculated energy levels of TTF^0 and TCNQ^0 molecules. For each irreducible representation of D_{2h} point group, the levels are labeled by serial numbers in order of increasing energy. Only a few of these serial numbers are actually shown. Unoccupied levels are shown by dashed line. The symbols σ and π refer to reflection with respect to the plane of the molecule.

and all other (occupied) levels contain 2 electrons. Having first established the ionization energy for A, one locates the position of level B (in Fig. 3) by subtracting the A-to-B excitation energy from the ionization energy of A. Thus, excitation energies in Fig. 3 can be read directly as the energy differences between solid and dashed lines. This is reminiscent of an energy-band-structure diagram, but it is clear from the above discription that electronic relaxation effects have been taken into account in our treatment. In practice, these relaxation effects are no larger than 0.1 or 0.2 eV for optical excitations in TCNQ and TTF. To test the internal consistency of our transition-state calculations, we tried to locate a particular excited level E by considering, independently, excitations from several initial levels A, B, C.... Each of these independent calculations usually led to the same position for excited level E to within 0.1 eV.

The energy levels in Fig. 3 are labeled by serial numbers in order of increasing energy for each irreducible representation of the D_{2h} point group. Only a few of the serial numbers are actually shown. The symbols σ and π at the bottom of Fig. 3 refer to reflection with respect to the plane of the molecule. The highest occupied and lowest unoccupied levels of TTF^0 are $4b_{1u}$ and $13a_g$, and of TCNQ^0, $3b_{1u}$ and $3b_{2g}$, respectively. It should be noted that the first ionization energies of TTF^0 and TCNQ^0 are 6.8 and 9.6 eV, respectively, according to recent photoemission measurements for TTF vapor[15] and TCNQ vapor.[16] Our theoretical models have been empirically adjusted to these experimental values. We believe that we have correctly identified[17-20] the highest occupied levels in these two molecules.

IV. ENERGY LEVEL STRUCTURE OF TCNQ$^-$ AND TTF$^+$

The energy levels for TCNQ$^-$ and TTF$^+$ calculated using the transition-state method are shown in Fig. 4 and are listed in Tables V and VI for completeness. For TCNQ$^-$ the orbital $3b_{2g}$ is singly occupied and $4b_{1u}$ is unoccupied. All ionization energies in TCNQ$^-$ have shifted upwards with respect to the corresponding values in TCNQ^0 by an amount ranging from 3.5 to 4.2 eV. The electron affinity of TCNQ^0 (which is the same as the ionization potential for TCNQ$^-$) is calculated to be 3.6 eV. This is to be compared with the experimental value[17] of 2.8 eV. Johansen[19] has reported a value of 2.6 eV recently. The two lowest optical transitions in TCNQ$^-$ are $3b_{1u} \rightarrow 3b_{2g}$ and $3b_{2g} \rightarrow 4b_{1u}$, which occur respectively at 2.0 and 2.5 eV and are polarized along the long molecular axis. The lowest transition qualitatively agrees with other theoretical calculations[18,19] but there is no general agreement for the next higher energy optical excitation.

All the calculated TTF$^+$ energy levels are shifted downwards with respect to the neutral spectrum by

TABLE III. Calculated ionization energies (eV) for TCNQ^0 molecule.

Orbital symmetry	a_g (σ)	b_{1g} (σ)	b_{2g} (π)	b_{3g} (π)	a_u (π)	b_{1u} (π)	b_{2u} (σ)	b_{3u} (σ)
	41.8(6)[a]	41.8(4)	13.7(1)	13.1(1)	13.1(1)	13.8(1)	41.8(4)	41.8(6)
	28.0(7)	20.9(5)	11.2(2)	10.0(2)		12.4(2)	25.7(5)	27.4(7)
	26.1(8)	19.4(6)	7.5[b](3)			9.4(3)	20.2(6)	23.2(8)
	22.4(9)	15.4(7)					17.8(7)	20.1(9)
	19.2(10)	14.4(8)					16.1(8)	16.2(10)
	16.8(11)	12.9(9)					15.4(9)	15.4(11)
	15.4(12)						12.9(10)	13.2(12)
	13.2(13)							

[a] The number in parentheses gives the serial number of the orbital in that symmetry.

[b] The affinity level.

TABLE IV. Calculated ionization energies (eV) for TTF^0 molecule.

Orbital symmetry	a_g (σ)	b_{1g} (σ)	b_{2g} (π)	b_{3g} (π)	a_u (π)	b_{1u} (π)	b_{2u} (σ)	b_{3u} (σ)
	26.4(7)[a]	22.6(6)	11.6(2)	10.2(2)	10.0(2)	12.2(2)	22.9(6)	26.1(7)
	24.3(8)	16.7(7)	8.3(3)			9.4(3)	17.6(7)	22.6(8)
	20.5(9)	12.2(8)				6.8(4)	13.1(8)	17.6(9)
	15.8(10)	10.7(9)					11.1(9)	14.0(10)
	14.3(11)							12.8(11)
	12.5(12)							

[a] The number in parentheses gives the serial number of the orbital in that symmetry.

an amount ranging from 4.1 to 4.6 eV. The orbital $4b_{1u}$ is singly occupied and has an ionization energy of 11.2 eV. Transition-state calculations for the three lowest-lying symmetry-allowed excitations yield $4b_{1u} \rightarrow 13a_g$ (2.0 eV, polarized along the axis perpendicular to the molecule), $4b_{1u} \rightarrow 4b_{2g}$ (3.2 eV, polarized along the long molecular axis), and $4b_{1u} \rightarrow 3b_{3g}$ (3.6 eV, polarized along the short molecular axis).

V. SIMPLIFIED CRYSTALLINE MODELS

Let us begin by considering a simplified model for solid TTF-TCNQ composed of TTF^+ and $TCNQ^-$ ions. We will neglect polarization effects and assume simply that when the crystal is formed, the energy levels for each constituent ion are shifted upwards or downwards by the Madelung potential produced by the ionic lattice. As an idealization, we will assume that the Madelung potential affects all orbitals on a given molecule equally, so that all the TTF^+ or $TCNQ^-$ levels are shifted rigidly by the same amount. We will also assume that the energy bands of interest have negligible width, and that the crystal is a semimetal with the Fermi level passing through the coincident narrow bands arising from the TTF^+ $4b_{1u}$ and $TCNQ^-$ $3b_{2g}$ levels. In the free ions, these levels lie at -11.2 and -3.6 eV, respectively, according to our calculations. In order to bring these two levels into coincidence, we shift the TTF^+ levels upwards in energy by 3.8 eV, and the $TCNQ^-$ levels downwards in energy by 3.8 eV. The superimposed and shifted energy-level structures for this model of TTF-TCNQ are shown in Fig. 5(c).

An alternate model is based on the idea that solid TTF-TCNQ is composed of neutral TCNQ and TTF molecules. If we simply superimpose the molecular-energy-level diagrams of $TCNQ^0$ and TTF^0 (cf. Fig. 3), we find that the highest occupied level for TTF^0 ($4b_{1u}$ at -6.8 eV) lies *above* the lowest unoccupied level for $TCNQ^0$ ($3b_{2g}$ at -7.5 eV). This situation is manifestly unphysical, since it would place an unoccupied energy band below an occupied one. Clearly, some charge transfer must take place in order to produce a physically acceptable solution.

If we consider a crystal formed from TTF^{+x} and $TCNQ^{-x}$ ions, where x is very small, we can produce a composite energy-level structure by superimposing the $TCNQ^0$ and TTF^0 energy levels, with the $3b_{2g}$ (lowest unoccupied) level of $TCNQ^0$ in registry with the $4b_{1u}$ (highest occupied level) of TTF^0, as indicated in Fig. 5(b). There is a paradox here, since the small charge transfer from TTF to TCNQ would produce Madelung shifts opposite in sign to that required to equilibrate the TCNQ $3b_{2g}$ and the TTF $4b_{1u}$ levels. As will be seen subsequently this paradox is removed once the charge transfer exceeds a threshold value of about 0.1 electron. Of course, the paradox arises because of the location

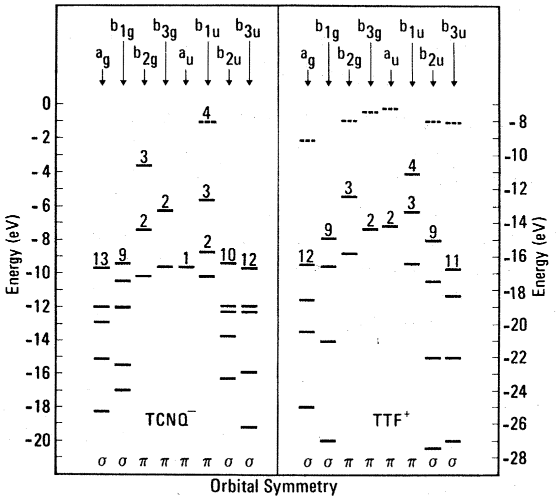

FIG. 4. Calculated energy levels of TTF^+ and $TCNQ^-$ ions. For each irreducible representation of D_{2h} point group, the levels are labeled by serial numbers in order of increasing energy. Occupied levels are denoted by solid lines, unoccupied levels by dashed lines. The ionization level ($4b_{1u}$) in TTF^+ is singly occupied and the affinity level ($3b_{2g}$) in $TCNQ^-$ is singly occupied. The symbols σ and π refer to reflection with respect to the plane of the molecule.

TABLE V. Calculated ionization energies (eV) for $TCNQ^-$ molecule.

Orbital symmetry	a_g (σ)	b_{1g} (σ)	b_{2g} (π)	b_{3g} (π)	a_u (π)	b_{1u} (π)	b_{2u} (σ)	b_{3u} (σ)
	37.6(6)[a]	37.6(4)	10.2(1)	9.6(1)	9.6(1)	10.2(1)	37.5(4)	37.6(6)
	23.9(7)	17.0(5)	7.4(2)	6.3(2)		8.7(2)	21.7(5)	23.2(7)
	21.9(8)	15.5(6)	3.6[b](3)			5.6(3)	16.3(6)	19.2(8)
	18.3(9)	12.0(7)					13.8(7)	15.9(9)
	15.1(10)	10.5(8)					12.3(8)	12.3(10)
	12.9(11)	9.5(9)					12.0(9)	12.0(11)
	12.0(12)						9.5(10)	9.70(12)
	9.7(13)							

[a] The number in parentheses gives the serial number of the orbital in that symmetry.

[b] Orbital $3b_{2g}$ is singly occupied in $TCNQ^-$.

of our isolated $TCNQ^0$ and TTF^0 levels. In any event, a small charge transfer leads to an energy-level structure which can be compared with that corresponding to TTF^+TCNQ^- [cf. Fig. 5(c)].

The two energy-level schemes shown in Figs. 5(b) and 5(c) differ from one another to the extent that the $TCNQ^0$ (TTF^0) levels are not shifted rigidly when the $TCNQ^-$ (TTF^+) ion is formed. The differential shifts are rather small, for the most part, so that there is a close resemblance between Figs. 5(b) and 5(c). If we could determine the electronic structure of TTF-TCNQ self-consistently, we could determine the charge transfer, the Madelung shifts, and also the polarization effects. We believe that such a calculation would lead to an energy-level structure similar to (and possibly intermediate to) those shown in Figs. 5(b) and 5(c).

VI. INTERPRETATION OF PHOTOEMISSION SPECTRUM OF SOLID TTF-TCNQ

We attempt to interpret the experimental photoemission spectrum[10] of solid TTF-TCNQ in terms of our energy-band model, which we take to be intermediate between those for TTF^0TCNQ^0 and TTF^+TCNQ^-. In Fig. 5(a) we have reproduced the experimental spectrum from Ref. 10. The highest experimental peak has been aligned with the highest occupied level (TTF $4b_{1u}$ and TCNQ $3b_{2g}$) on the assumption that this peak is produced by photoemission from the highest occupied bands in the solid. This leads to a reasonable correspondence between the remainder of the experimental spectrum (except the next to the highest peak) and the theoretical energy-level structure. For example, there are a large number of theoretical energy levels in the vicinity of the main experimental peak.

Assuming the validity of our theoretical energy-level scheme, we must now account for the next to the highest experimental peak, which does not correspond to any of our theoretical levels. Since most of the photoemission takes place at or near the surface, it is reasonable to seek an explanation for the next to the highest peak in terms of a special feature associated with the TTF-TCNQ surface.

After considering various possibilities, we have come to the conclusion that the next to the highest peak could well be due to emission from neutral molecules of one species lying above a chain of molecules of the other species, for example, a $TCNQ^0$ molecule lying above a TTF^{+x} chain or a TTF^0 molecule lying above a $TCNQ^{-x}$ chain. The proposed model is shown schematically in Fig. 6. To establish the plausibility of such a model, we note that in the interior of the crystal, the Madelung potential is negative for a $TCNQ^{-x}$ ion, and positive for a TTF^{+x} ion. In Fig. 7 we have located

TABLE VI. Calculated ionization energies (eV) for TTF^+ molecule.

Orbital symmetry	a_g (σ)	b_{1g} (σ)	b_{2g} (π)	b_{3g} (π)	a_u (π)	b_{1u} (π)	b_{2u} (σ)	b_{3u} (σ)
	30.8(7)[a]	27.1(6)	15.8(2)	14.5(2)	14.3(2)	16.5(2)	27.4(6)	30.4(7)
	28.8(8)	21.1(7)	12.5(3)			13.6(3)	22.1(7)	27.1(8)
	25.1(9)	16.7(8)				11.2[b](4)	17.5(8)	22.2(9)
	20.4(10)	14.9(9)					15.2(9)	18.3(10)
	18.7(11)							16.8(11)
	16.6(12)							

[a] The number in parentheses gives the serial number of the orbital in that symmetry.

[b] Orbital $4b_{1u}$ is singly occupied in TTF^+.

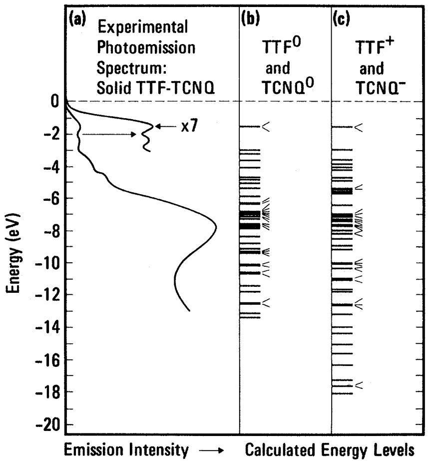

FIG. 5. Comparison of theoretical and experimental spectra: (a) experimental photoemission spectrum reproduced from Ref. 10; (b) superposition of TCNQ^0 and TTF^0 molecular energy levels; (c) superposition of TCNQ$^-$ and TTF$^+$ molecular energy levels.

the positions of the relevant energy levels for the isolated molecules for zero and unity charge transfer, and drawn straight lines (shown by dot-dash) connecting the end points to indicate the intermediate behavior. The Fermi level is then determined by the center of gravity of these two lines, corresponding to the coincidence of the TCNQ^{-x} $3b_{2g}$ and the TTF^{+x} $4b_{1u}$ levels. The vertical separation between the isolated molecular levels and the Fermi level is a measure of the Madelung shift at any particular value of x. For example, the Madelung shift for TCNQ$^{-1/2}$ is -1.9 eV (downward shift) and that for TTF$^{+1/2}$ is $+1.9$ eV (upward shift). It can be seen from Fig. 7 that the Madelung shift for unity charge transfer is 3.8 eV, as we have noted earlier. Note also that as soon as the charge transfer exceeds ~0.1 electron, the Madelung shifts for TCNQ^{-x} and TTF^{+x} have the appropriate signs and the paradox mentioned earlier disappears.

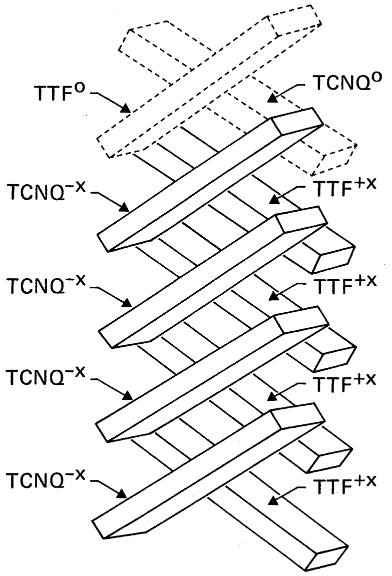

FIG. 6. Schematic diagram of the proposed molecular model for explaining the next to the highest photoemission peak in the (TTF) (TCNQ) spectra. The neutral surface molecules are denoted by dashed lines, whereas the bulk chains including their end members are denoted by solid lines.

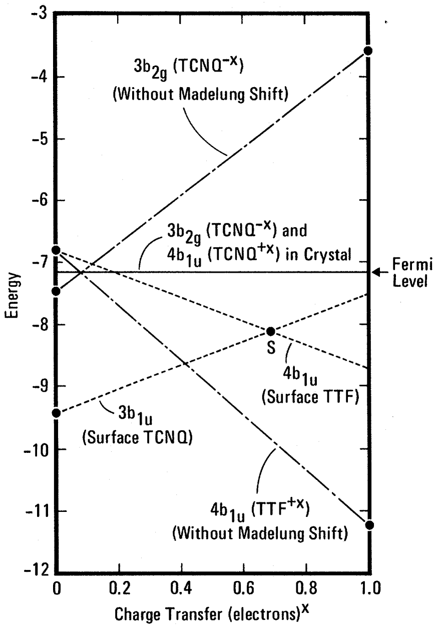

FIG. 7. Variation of selected energy levels with charge transfer. The interpolated energy levels for the isolated molecules are shown by dash-dotted lines. When these levels occur in the bulk (in TTF^{+x} and TCNQ^{-x} chains) they are subjected to Madelung shifts which equilibrate the TTF^{+x} $4b_{1u}$ and TCNQ^{-x} $3b_{2g}$ levels and thereby define the Fermi level (shown by solid line). The levels associated with neutral surface molecules are shown by dashed lines. These levels are subjected to reduced Madelung shifts as explained in the text.

For simplicity we assume that all the energy levels associated with a given molecular position in the bulk suffer the same Madelung shift. Moreover, we assume that the Madelung shift is substantially the same for the end member of a chain as for an interior member. Finally, we assume that the Madelung shift for a molecule lying just above the chain is equal to half the Madelung shift for the interior (and end) of the chain. The Fermi level of Fig. 7 is aligned with the highest experimental peak and we are seeking an explanation for the next to the highest peak ~1 eV below it. If we now visualize a neutral TCNQ molecule placed right next to the TTF^{+x} molecule at the surface (see Fig. 6) we can expect this TCNQ molecule to experience a Madelung shift about half as large as a TTF^{+x} molecule experiences in the bulk, i.e., an *upward* shift. The Madelung-shift-corrected $3b_{1u}$ level for a surface TCNQ molecule is shown in Fig. 7. For $x\sim 0.7$ this level would lie about 1 eV below the Fermi level (see point *S*). Emission from this highest occupied *surface* $TCNQ^0$ orbital would account for the next to the highest experimental peak.

A similar analysis can be made for a TTF^0 molecule lying next to a $TCNQ^{-x}$ molecule on the surface. The Madelung shift for the TTF^0 molecule would be about half that for a $TCNQ^{-x}$ molecule in the bulk, namely, a downward shift. The highest occupied level for the TTF^0 molecule ($4b_{1u}$) would lie about 1 eV below the highest occupied bulk levels for $x\sim 0.7$, approximately where we placed the highest occupied level for the surface $TCNQ^0$ molecule in the preceding discussion. Emission from the highest occupied surface TTF^0 molecule could also account for the next to the highest experimental peak. Since we cannot resolve emission from $TCNQ^0$ and TTF^0 molecules on the surface, either only one of these species actually lies on the surface, or the charge transfer is about $x=0.75$, which will lead to a coincidence of the emission peaks from $TCNQ^0$ and TTF^0 on the surface.

To recapitulate, the next to the highest experimental peak is attributed to emission from a surface $TCNQ^0$ molecule lying next to a TTF^{+x} chain, or a surface TTF^0 molecule lying next to a $TCNQ^{-x}$ chain. The highest experimental peak is attributed to emission from bulk or surface TTF^{+x} and $TCNQ^{-x}$ molecules. The remaining experimental spectrum can be attributed to transitions from bulk $TCNQ^{-x}$ and TTF^{+x} molecules, as well as from $TCNQ^0$ and TTF^0 molecules at the surface. According to our model, a substantial fraction of the chains have a neutral molecule of the opposite species above them. Weak charge-transfer complexes probably form between the end $TCNQ^{-x}$ (or TTF^{+x}) and the adjacent TTF^0 (or $TCNQ^0$) molecule.

ACKNOWLEDGMENTS

The authors are pleased to acknowledge fruitful conversations and correspondence with Professor K. H. Johnson, Dr. W. E. Rudge, Dr. B. H. Schechtman, and Dr. P. S. Bagus.

---

[1] See, for example, I. F. Shchegolev, Phys. Status Solidi A 12, 9 (1972); J. Ferraris, D. O. Cowan, V. Walatka, Jr., and J. H. Peristein, J. Am. Chem. Soc. 95, 948 (1973); A. J. Epstein, S. Etemad, A. F. Garito, and A. J. Heeger, Phys. Rev. B 5, 952 (1972); L. B. Coleman, J. J. Cohen, D. J. Sandman, F. G. Yamagishi, A. F. Garito, and A. J. Heeger, Solid State Commun. 12, 1125 (1973); and subsequent papers.

[2] F. Herman and I. P. Batra, Phys. Rev. Lett. 33, 94 (1974).

[3] F. Herman and I. P. Batra, Nuovo Cimento B 23, 282 (1974).

[4] B. I. Bennett and F. Herman, Chem. Phys. Lett. (to be published).

[5] D. A. Liberman (unpublished); N. Rösch, W. G. Klemperer, and K. H. Johnson, Chem. Phys. Lett. 23, 149 (1973); N. Rösch and K. H. Johnson, *ibid.* 24, 175 (1974); I. P. Batra and O. Robaux, *ibid.* 28, 529 (1974).

[6] F. Herman, A. R. Williams, and K. H. Johnson, J. Chem. Phys. 61, 3508 (1974).

[7] K. H. Johnson, J. Chem. Phys. 45, 3085 (1966); J. C. Slater, Adv. Quantum Chem. 6, 1 (1972).

[8] K. H. Johnson, Adv. Quantum Chem. 7, 143 (1973); D. A. Liberman and I. P. Batra, J. Chem. Phys. 59, 3723 (1973).

[9] K. H. Johnson, J. G. Norman, Jr., and J. W. D. Connolly, in *Computational Methods for Large Molecules and Localized States in Solids*, edited by F. Herman, A. D. McLean, and R. K. Nesbet (Plenum, New York, 1973), p. 161; K. H. Johnson and F. C. Smith, Jr., MIT Scattered Wave Computer Program, 1972 (unpublished); D. A. Liberman and I. P. Batra, IBM Res. Rept. No. RJ 1224 (May 1973) (unpublished).

[10] W. D. Grobman, R. A. Pollak, D. E. Eastman, E. T. Maas, Jr., and B. A. Scott, Phys. Rev. Lett. 32, 534 (1974).

[11] T. J. Kistenmacher, T. E. Phillips, and D. O. Cowan, Acta Crystallogr. B 30, 763 (1974). The C–H bond length was assumed to be 1.09 Å (representative neutron scattering value). The C–H bond was assumed to make equal angles with the C=C and C=S bonds.

[12] R. E. Long, R. A. Sparks, and K. N. Trueblood, Acta Crystallogr. 18, 932 (1965) (TCNQ crystal). The C–H bond distance was taken as 109 Å.

[13] F. A. Cotton, *Group Theory with Chemical Applications*, 2nd ed. (Interscience, New York, 1971).

[14] J. C. Slater and K. H. Johnson, Phys. Rev. B 5, 844 (1972).

[15] R. Gleiter, E. Schmidt, D. O. Cowan, and J. P. Ferraris, J. Elec. Spectrosc. Rel. Phenom. 2, 207 (1973).

[16] J. N. A. Ridyard (private communication). The TCNQ vapor spectrum was obtained with Perkin-Elmer Model PS 18.

[17] C. E. Klots, R. M. Compton, and V. F. Raaen, J. Chem. Phys. 60, 1177 (1974).

[18] H. T. Jonkman, G. A. van der Velde, and W. C. Nieuwpoort, Chem. Phys. Lett. 25, 62 (1974); H. T. Jonkman and J. Kommandeur, *ibid.* 15, 496 (1972).

[19] H. Johansen, Theor. Chim. Acta (to be published).

[20] B. H. Schechtman, S. F. Lin, and W. E. Spicer, Phys. Rev. Lett. 34, 667 (1975).