Abstract submitted

for the Berkeley Meeting of the

American Physical Society

27-29 December 1973

Reflectance of Conducting TCNQ Salts. G. C.
WRIGHTON, Stanford U.; P. M. GRANT, R. L. GREENE and
G. CASTRO, IBM Research, San Jose.--The polarized
single crystal reflectance of three conducting salts-
(TTF)(TCNQ), (NMP)(TCNQ) and (TEA)(TCNQ)$_2$ has been
measured over the energy range 0.5-5 eV and temperature
range 20-300 °K. The optical constants have been
determined by Kramers-Kronig analysis. The compounds
have similar optical properties, namely, (1) a Drude-
like edge around 0.7 eV when the incident electric
field is polarized parallel to the conducting axis,
(2) a doublet at 1.3 eV, and (3) a wide peak at about
3.5 eV. The latter peaks are observed in both the
parallel and perpendicular directions; however, the
doublet is better resolved in parallel polarization.
All structure shifts to higher energies with lowering
temperature. The doublet and the 3.5 eV peak agree
with the solution spectra of the (TCNQ)$^-$ ion and this
suggests strong charge transfer. The unusual occurrence
of a Drude-like edge in each material at nearly identi-
cal energies contrasted with conductivities which vary
by two orders of magnitude will be discussed.

Submitted by

Glenn C. Wrighton
Physics Department
Stanford, California

bulletin

OF THE AMERICAN PHYSICAL SOCIETY

1 DECEMBER 1973

1973 WINTER MEETING IN THE WEST
IN BERKELEY, CALIFORNIA
27–29 DECEMBER 1973

BD 8 Intercalation vs. Extercalation in Ternary Graphite Compounds.* L. B. EBERT[†], R. A. HUGGINS, and J. I. BRAUMAN, Stanford U. --Recent studies[1] have shown that certain properties ascribed to intercalated molecules in graphite actually arise from surface bound material. NMR studies have been completed on two graphite-phosphoric acid-chromium trioxide compounds, one with predominant surface binding species and the other containing only intercalated molecules. Simultaneous motional narrowing of both ^1H and ^{31}P above 225 K indicates a high mobility of phosphoric acid in both compounds. Previous work of Ubbelohde[2] and Vučelić[3] is used in interpreting these results in terms of an ionic and molecular substructure.

[1]L. B. Ebert, R. A. Huggins, and J. I. Brauman, submitted to Carbon.

[2]A. R. Ubbelohde, Proc. R. Soc. Lond. A 327, 289 (1972).

[3]D. Vučelić and M. Huter, Chem. Phys. Lett. 19, 448 (1973).

BD 9 Extrinsic Electroabsorption in Crystalline and Amorphous Semiconductors.* A.D.JONATH, E.VORONKOV** and R.H.BUBE, Stanford U.--A detailed investigation of extrinsic electroabsorption has been carried out in single crystal GaAs:O for photon energies much less than the bandgap. For a crystal with $300^\circ K$ Fermi level 0.54 eV below the conduction band, 11 major peaks are observed between 0.52 and 1.39 eV, using apparatus capable of measuring a field-induced change in absorption coefficient as small as 10^{-5} cm^{-1}. Variations of structure with light polarization, detection frequency and phase angle, applied field, temperature and pre-illumination were detected. Both first harmonic (signal linear with field) and second harmonic (signal quadratic with field) spectra were observed, indicating both permanent and induced defect dipole moments. Both first and second harmonic spectra were also measured for amorphous As_2SeTe_2 with structure between 0.47 and 0.90 eV, compared to a 1.0-eV bandgap.

BD 10 Photoemission Study of the Effect of Oxidation on Direct Transitions in Copper.* L. F. WAGNER and W. E. SPICER, Stanford U. --The oxidation of copper prepared by evaporation under ultrahigh vacuum conditions has been studied by ultraviolet photoemission. Upon initial contact with oxygen the copper surface undergoes a rapid 0.2 eV increase in work function. This is followed by slow structure changes in the electron energy distributions which are associated with the formation of bulk Cu_2O as the oxygen diffuses into the copper lattice. Two of these changes, the formation of a bandgap and the development of a low energy oxygen associated peak, are expected. However, in addition it is found that a strong structure in the energy distribution is preferentially decreased by the oxygen exposure. In order to establish more firmly the bulk nature of the optical transitions, high resolution energy distributions for clean Cu are shown to agree with calculations when a photon energy dependent term is taken into account.

BD 11 Electron Irradiation Effects in MOS Systems: Experimental Data with a Proposed New Model. J. N. CHURCHILL, Univ. of Calif., Davis, T. W. COLLINS, International Business Machines Corporation, F. E. HOLMSTROM, Calif. State Univ., San Jose. -- MOS capa-

citors were irradiated with 18 kev electrons and the shifts in characteristic C-V curves were studied to clarify certain aspects of published experimental data and their accompanying models. Comparison of the flat-band shift versus gate bias during electron irradiation yielded curves which show four distinct regions for capacitors having a 500 Å thick SiO_2 oxide on p-type Si. Most noteworthy on the curves are two linear regions for small gate biases separated by a non-zero minimum shift which occurred for a negative gate bias. For larger gate biases (positive or negative), the flat-band shift remained constant. To explain these observations, we propose a model based on a consistent treatment of energy bands at the Al gate contact as well as at the oxide-semiconductor interface. A computer simulation of this model is in excellent agreement with all regions of the experimental data for all positive and negative gate bias values.

BD 12 Spectroscopic Studies of Gamma Irradiated Single Crystals of $Co^{2+}/KMgF_3$*. N.H. AKED and DAVID J. SIMKIN, McGill U.-- The optical absorption, ESR and MCD spectra of KMg(Co)F_3 following gamma irradiation, were measured. The results show that the presence of the Co(II) ions in the crystal suppresses production of F centers, but is at the same time responsible for the appearance of several new color centers, not found in the undoped crystals. The oxidation state of the Co is found to remain unchanged by the gamma irradiation. Two of the new bands which arise in the visible spectrum are ascribed to F aggregate centers, while the remainder arise from a new center or centers of unknown structure, but probably involving the impurity Co ions. Fine structure which appears on one of the bands at 4.2 °K can be assigned to vibrational interactions between the color center and the lattice.

BD 13 Lattice Defects in Annealed GaAs Single Crystals.* S.Y. CHIANG and G.L. PEARSON, Stanford U. — Undoped boat-grown GaAs n-type single crystals were annealed at 700-$1000^\circ C$ in vacuum and at selected As overpressure. Carrier concentration versus depth was then measured using the Schottky barrier technique while successively etching away thin surface layers. Two types of defects were observed, donors of high concentration near the surface and acceptors of lower concentration extending further into the crystal. The donors were depressed and the acceptors enhanced with increasing arsenic pressure. From these results and thermodynamic considerations, we conclude that donors are associated with arsenic vacancies and acceptors with gallium vacancies, both of which form at the surface and diffuse into the crystal. The diffusivity D of the donor and acceptor defects is $D = 7.9 \times 10^3$ $exp(-4.0/kT)$ and $D = 2.1 \times 10^{-3}$ $exp(-2.1/kT)$ respectively. Photoluminescence studies show that both types of defects form non-radiative levels.

BD 14 Reflectance of Conducting TCNQ Salts. G. C. WRIGHTON, Stanford U.; P. M. GRANT, R. L. GREENE and G. CASTRO, IBM Research, San Jose.--The polarized single crystal reflectance of three conducting salts-(TTF)(TCNQ), (NMP)(TCNQ) and (TEA)(TCNQ)$_2$ has been measured over the energy range 0.5-5 eV and temperature range 20-300 °K. The optical constants have been determined by Kramers-Kronig analysis. The compounds have similar optical properties, namely, (1) a Drude-

like edge around 0.7 eV when the incident electric field is polarized parallel to the conducting axis, (2) a doublet at 1.3 eV, and (3) a wide peak at about 3.5 eV. The latter peaks are observed in both the parallel and perpendicular directions; however, the doublet is better resolved in parallel polarization. All structure shifts to higher energies with lowering

temperature. The doublet and the 3.5 eV peak agree with the solution spectra of the $(TCNQ)^-$ ion and this suggests strong charge transfer. The unusual occurrence of a Drude-like edge in each material at nearly identical energies contrasted with conductivities which vary by two orders of magnitude will be discussed.

Supplementary Program

BD 15 RAMAN SCATTERING BY SURFACE POLARITONS II. EXPERIMENT. Y.J.CHEN, S.P.B.BUCHNER AND E.BURSTEIN. U. of Penna. -- We have observed Raman scattering by surface polaritons (sπ) at the interface of an epitaxial film of GaP (d=22μ) on a (100) GaAs substrate* in which the GaP served as the surface and non-linear active medium. The experiments were carried out using 5145Å excitation radiation for which the skin depth δ in GaP is 34μ, and 4880Å for which δ is 10μ. The observed peaks correspond to the low frequency slab modes. Since bulk polariton modes also appear in the spectra, we conclude

that the slab mode peaks correspond to forward scattering of theincident radiation which is reflected from the GaAs-GaP interface. In related experiments on (110) GaAs-air and GaAs-saphire single interfaces, for which backscattering by LO phonons is forbidden, no scattering by sπ or the LO mode in perpendicular polarization was observed using 4880 Å excitation radiation.

*Kindly supplied by A.E.Blakeslee, I.B.M.

THURSDAY AFTERNOON, 27 DECEMBER 1973

(ALLAN N. KAUFMAN presiding)

General Theory

BE 1 Experimental Distinction Between the Quantum and Classical Field Theoretic Predictions for the Photoelectric Effect* J. F. CLAUSER, Univ. of Calif., Berkeley.--It has been earlier shown that previous experimental observations of the photoelectric effect do not exclude a semiclassical description without the auxiliary constraint of microscopic energy conservation (as opposed to macroscopic, statistical energy conservation). We report here an experiment in which this conservation is observed and not assumed. Previous experiments do not do this. The scheme involved a comparison of various twofold coincidence rates between four photomultiplier tubes viewing cascade optical photons emitted through various beam-splitters. The results, with no further assumptions, to high statistical accuracy contradict the predictions by any classical or semiclassical radiation theory in which the probability of photoemission is proportional to the classical field intensity.

*Work supported by the A.E.C.

BE 2 The Electron-Positron Lattice. M. SIMHONY, Elect. Dept., Col. of Eng. & Appl. Sc., U. of Wisconsin-Milwaukee, and Racah In. of Phys., Hebrew U., Jerusalem, Israel.-- It is postulated that a three-dimensional lattice of electrons and positrons (epola), similar to ionic lattices, permeates the universe. The epola is subject to the electromagnetic (em) field, thus not an aether. It is shown that epolar deformation waves are detected as em waves and have the same velocity c. With the mass m_e of the electron, its distance to neighbor positrons is found 4.4×10^{-15}m and the binding energy $m_e c^2$. Thus creation of a free electron-positron pair is its sublimation from the massless epola, and annihilation is entrapment. With epolar concepts, formulas postulated by other theories become deriveable. So, the energy-frequency relation for photons is derived using the Compton wavelength. De Broglie wavelength is obtained as that of the accompanying epolar wave (aew) of a moving particle. Then Bohr's orbits are obtained with the request of energy conservation in the system "particle ↔ aew",

and the dependence of mass on velocity-as a result of momentum conservation in this system. Interpretation of known experiments and some new ones are proposed.

BE 3 Symmetry as a Quantitative Observation. R. C. SILL, Physics Dept., Univ. of Nevada, Reno and J. L. FINNEY, Crystallography Dept., Birkbeck Coll., Univ. of London.--It is sometimes possible to determine symmetry response without ambiguity where precise functional dependence may be out of reach of available or even extant state of the art instrumentation. Attention to symmetry even can lead to surprising depth of explication of the phenomena. An extraordinarily common phenomenon will be discussed from this point of view. It is a review of the behavior of a rotating translating flat object like a square of postboard. Symmetry observations lead to predictions of stable and unstable states which can be confirmed, and permit identification of a force which leads to a torque acting on the object that has the form

$$\vec{\Gamma} = C \frac{I v^2}{\omega^2} \left(\frac{\vec{g}}{g}\right) \times \left(\frac{\vec{v}}{v}\right)$$

where $\vec{\Gamma}$ is torque; I, moment of inertia; $\vec{v}$, velocity of translation; $\vec{\omega}$, angular velocity of rotation; $\vec{g}$, acceleration of gravity, and C is a dimensional factor with units $L^{-2}T^{-2}$. Further specification of the relation calls for detailed measurements of the system in a wind tunnel.

BE 4 Gauge-Invariant Y-M Operators Coupled to the Spinor-Isospinor Field. Richard P. Treat, West Virginia U.-- Gauge-invariant (-scalar) Y-M and spinor-isospinor variables are constructed which are functionals of the usual local Y-M potentials. These operators are a generalization of the operators employed by Dirac[1] in a gauge-invariant formulation of quantum electrodynamics. A gauge-invariant decomposition of the Y-M potentials into an isovector and an integrable part permits a construc-

We have measured the polarized single crystal reflectance of a number of tetracyanoquinodimethane (TCNQ) salts from energy .5-5 eV and from temperature 16-300°K. They include salts with TCNQ complexed with tetrathiofulvaninium TTF(TCNQ), n-methyl-phenazinium (NMP)(TCNQ), and triethylammonium TEA(TCNQ)$_2$. The salts are characterized by stacked chains of TCNQ and by relatively high anisotropic conductivity. TTF(TCNQ) and NMP(TCNQ) are metal-like at room temperature and undergo a metal-insulator transition at 60° and 250°K respectively while TEA(TCNQ)$_2$ shows an activated conductivity up to room temperature. The conductivity of TEA(TCNQ)$_2$ is two orders of magnitude less than TTF(TCNQ) at room temperature.

Figure I shows the reflectance of all the salts at room temperature when the electric vector is polarized parallel to the conducting axis. First note that all the salts show a reflectance edge in the region .5-1 eV. This edge is certainly related to the conduction properties of the salts. Since we have no data below .5 eV we cannot determine whether this edge indicates an activated charge transfer band or a Drude metal. Our data does say that the gap is less than .5 eV which is in agreement with the conductivity data.

Now consider the energy region above the edge. The reflectance data shows some striking similarities. There is a doublet at about 1.3 eV and a peak at 3.5 eV in every case. There is also some additional structure in TTF(TCNQ) and TEA(TCNQ)$_2$.

The reflectance of these salts when the electric vector is perpendicular to the conducting axis shows the visible structure of the parallel case but does not show the low energy edge. When the temperature is lowered from 300°K to 16°K the spectra undergoes a general blue shift af about .1 eV. There is no dramatic change in the reflectance edge.

In Figure II we return to consideration of the visible properties of these complexes. Here the parallel reflectance of TTF(TCNQ) is plotted with the absorption data of TCNQ⁻ as seen in solution. Note that the doublet and the 3.5 eV peak in the reflectance can be associated with the solution spectra. The solution spectra of $TCNQ^0$ and $TCNQ^{-2}$ show no structure near 1.3 eV, and we believe that the existence of this doublet implies a significant amount of charge transfer from the cation to the TCNQ in all of these salts. This is in agreement with some recent photoemission work done on TTF(TCNQ) by Grobmann et al. at IBM Yorktown.

Further literature work shows that the other structural details, with the exception of the 2 eV peak, can be matched to the appropriate cation solution spectra. This suggests that there may be some physical significance to fitting the reflectance with a sum of Lorentzian oscillators in order to determine the optical constants. Also this procedure should be more reliable than Kramers-Kronig analysis because the reflectance is increasing above our data, indicating strong transitions there.

Figure III indicates our fitting procedure. The dielectric constant ε is written as a sum of Lorentzian oscillators. We place one oscillator at zero energy to fit the low energy edge and include other oscillators to fit the visible structure. From this ε we can determine a calculated reflectance. We vary the parameters ε_0, ω_{o_j}, ω_{p_j} and τ_j so as to determine the best fit with the reflectance data. Having determined the optical constants we can calculate the optical absorption $\alpha = 4\pi k/\lambda$. Figure IV shows a typical fit of the data. Figure V shows the calculated absorption α for the parallel case in TTF(TCNQ) plotted with the solution absorbance. Note that there is a significant difference in the ratio of the absorption as seen in solution compared to the solid state. This may occur because in polarized reflectance we are

looking at a particular direction and not the averaged situation as seen in solution spectra. It might also happen if there is only partial charge transfer; or if transition strength is transferred to other transitions which become stronger in the solid state.

Figure VI shows the imaginary part of the dielectric constant ϵ_2 for each individual oscillators in TTF(TCNQ) parallel polarization case. Since the oscillator are relatively narrow and distinct it makes sense to identify the oscillators as transitions. The peak S_3 at 2.9 eV can be associated with the TTF^+ ion.

To explain the other transition refer to the molecular orbital diagrams. The single particle states of TCNQ were furnished by Batra and Hermann in a private communication. S_1 the doublet at 1.3 eV is a $b_{1u} \rightarrow b_{2g}$ transition observed in both the anion and the solid state. The peak at 3.4 eV is also seen in both states and is a $b_{2g} \rightarrow b_{1u}$ transition. The $S_0{}^{11}$ edge can easily be explained as a charge transfer transition or an interband transition. S_2 is somewhat a mystery, it cannot be directly connected to solution spectra yet it appears in all stacked TCNQ salts. It may be an excited state charge transfer state and we have tentatively assigned it that way, $b_{2g} \rightarrow b_{3u}$ transition.

In conclusion, we find that TEA(TCNQ)$_2$, TTF(TCNQ) and NMP(TCNQ) all have a low energy charge transfer band probably associated with its conductivity. Further we find that the salts retain the basic characteristics of localized states in the visible region and these transitions strongly support charge transfer between the cations and TCNQ.
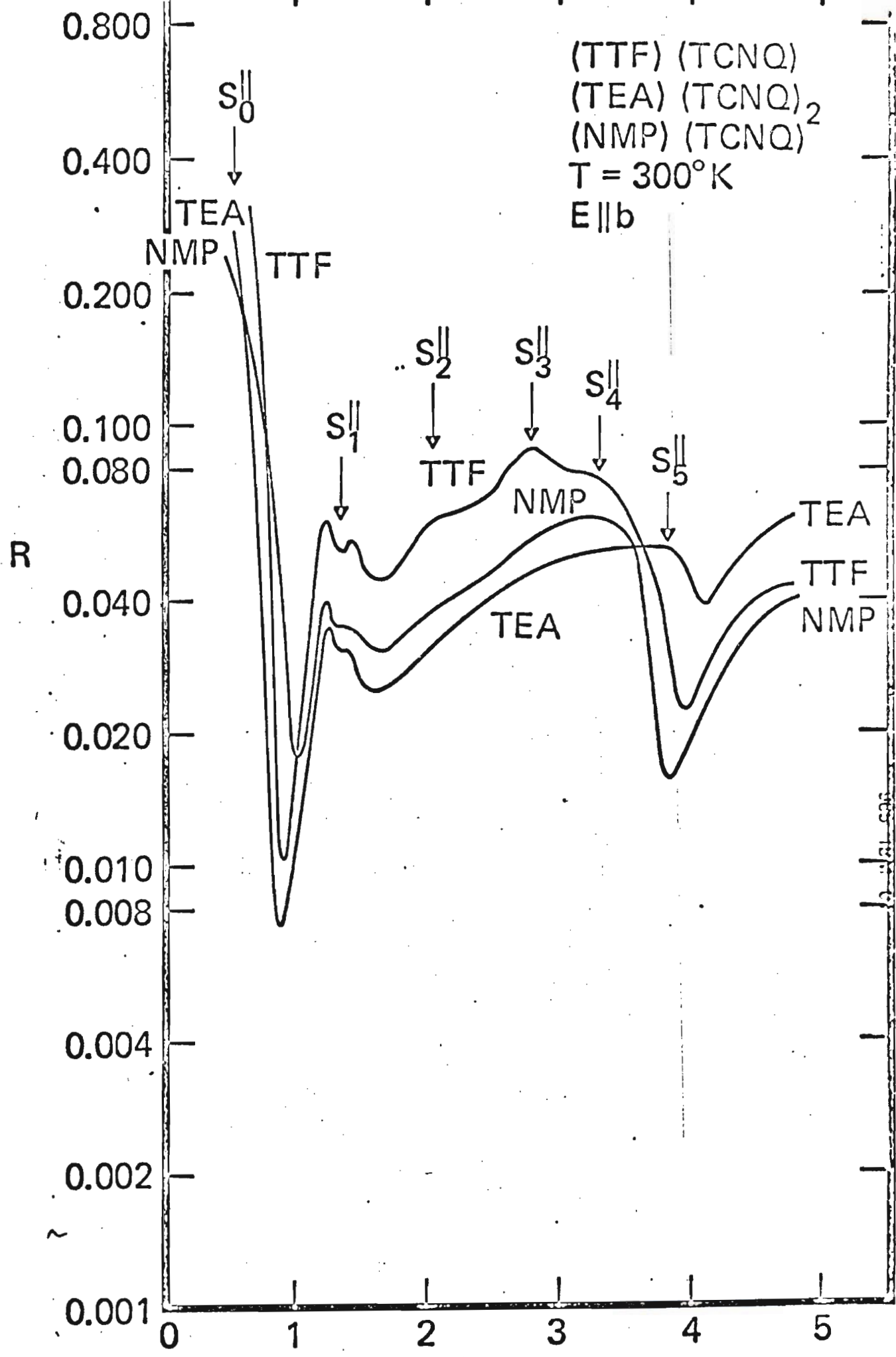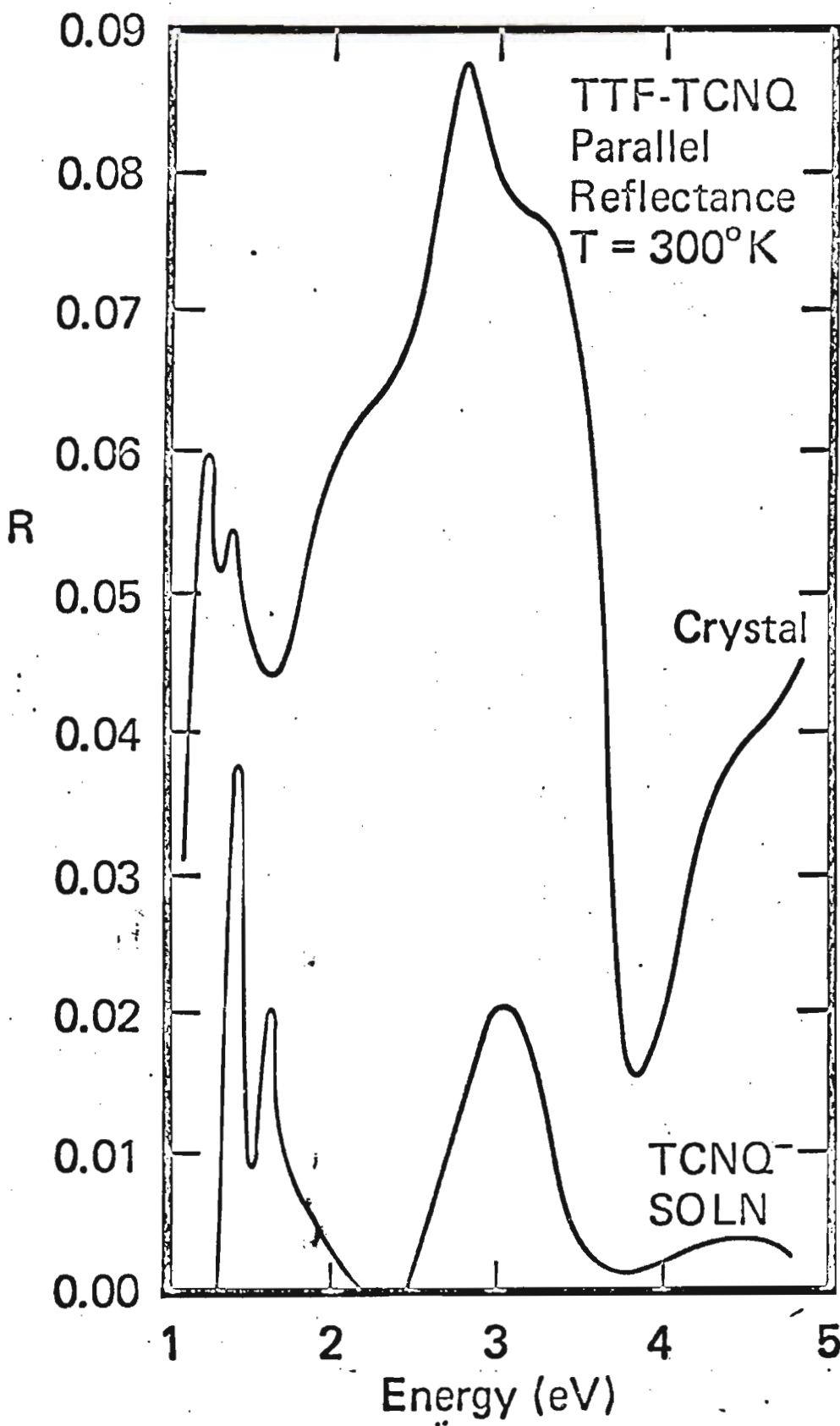
Fig. I

(TTF) (TCNQ)
(TEA) (TCNQ)$_2$
(NMP) (TCNQ)^2
T = 300° K
E ‖ b

Fig. II

TTF-TCNQ
Parallel
Reflectance
T = 300°K

Crystal

TCNQ
SOLN

R

Energy (eV)

965 · IBM · 01

Fig. 111

Summary of Fitting Technique

$$\epsilon(\omega) = \epsilon_1 + i\epsilon_2 = \epsilon_0 + \sum_{j=1}^{N} \frac{\omega_{pj}^2}{(\omega_{0j}^2 - \omega^2) + \frac{i\omega}{\tau_j}}$$

$$n = \left\{ \frac{\epsilon_1}{2} + 1/2 \left[\epsilon_1^2 + \epsilon_2^2\right]^{1/2} \right\}^{1/2}$$

$$k = \left\{ -\frac{\epsilon_1}{2} + 1/2 \left[\epsilon_1^2 + \epsilon_2^2\right]^{1/2} \right\}^{1/2}$$

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2}$$

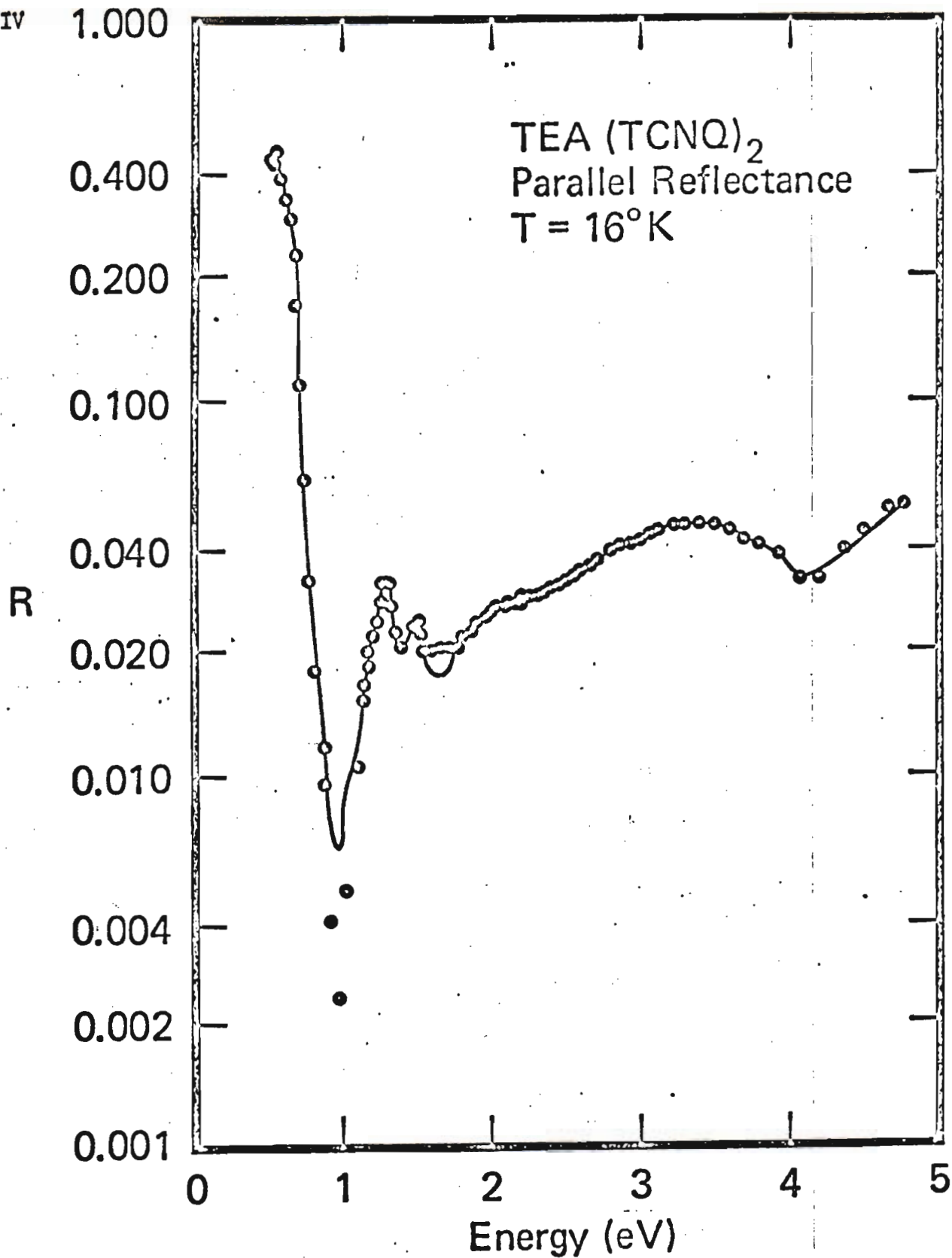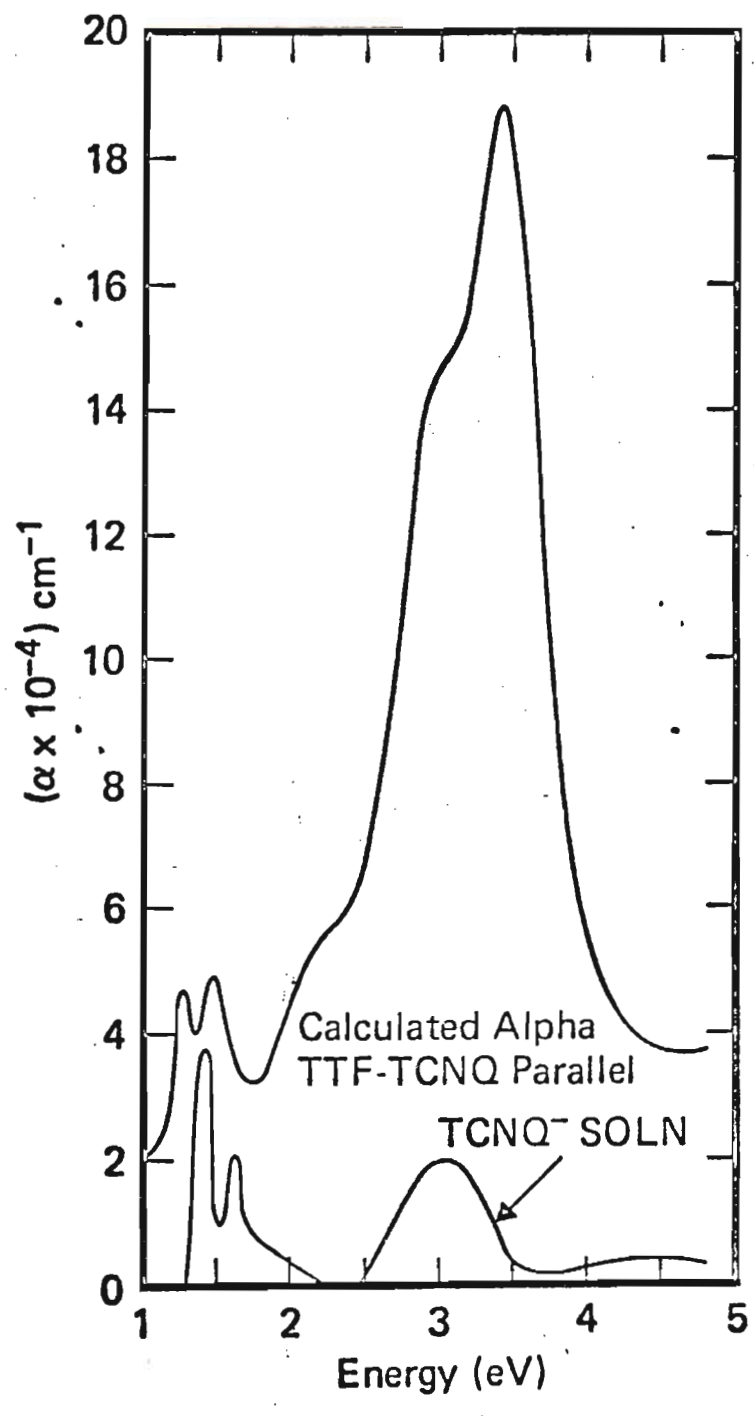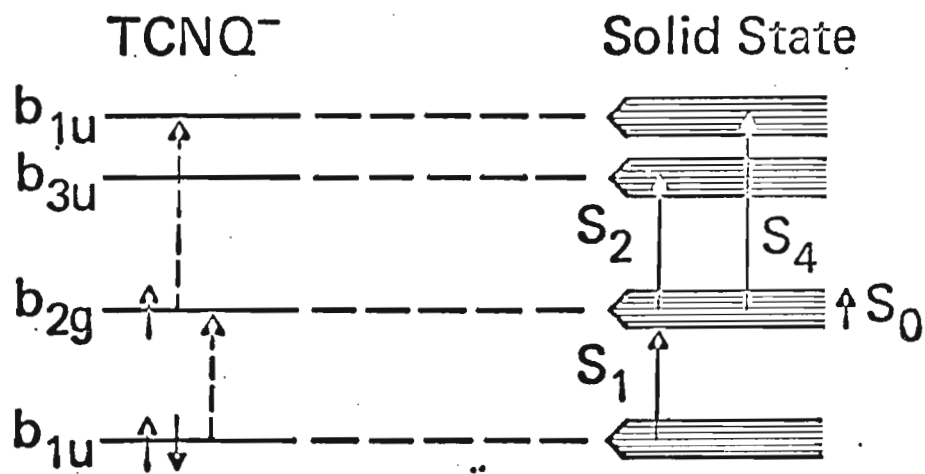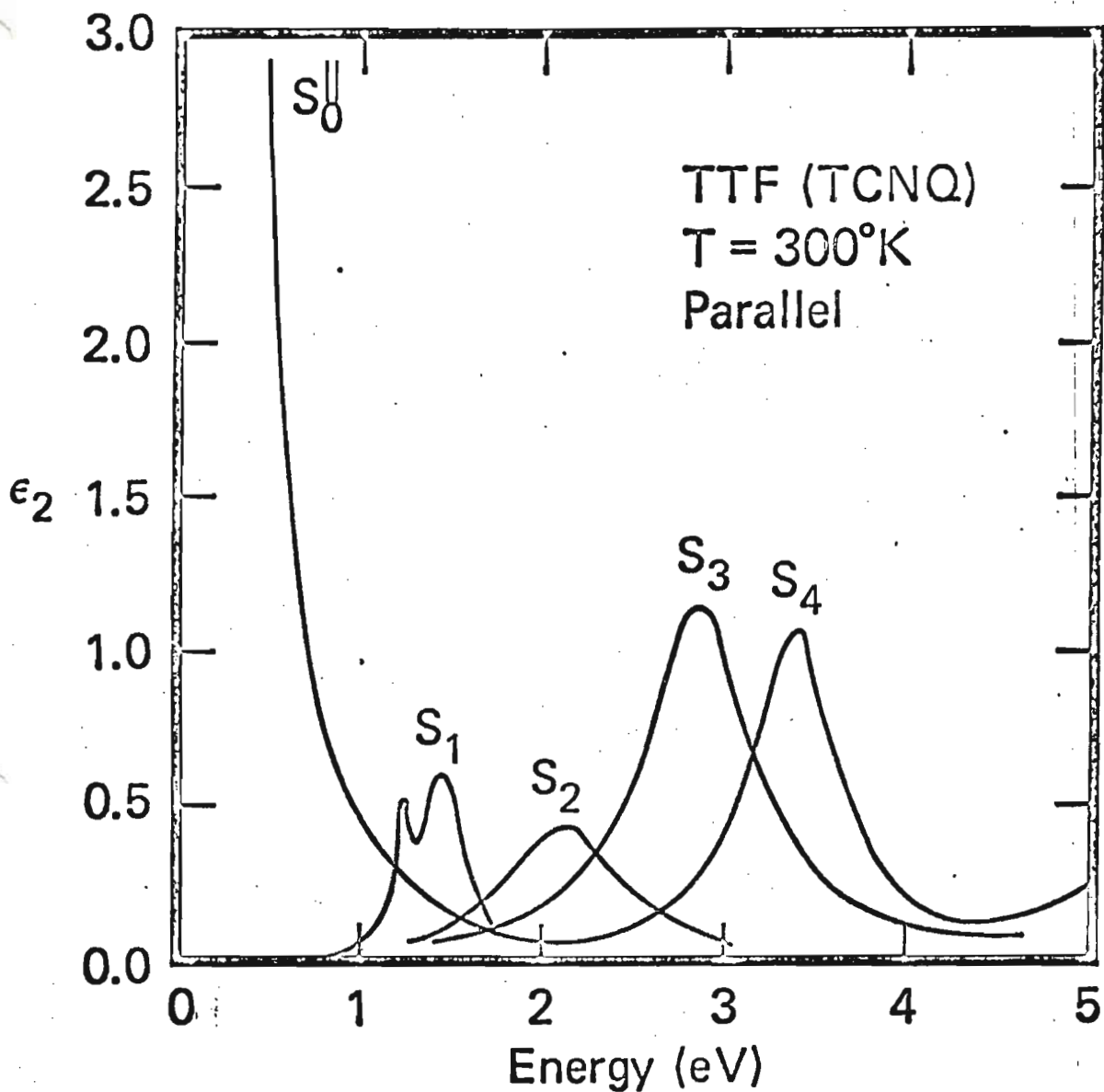$$\text{Absorption } \alpha = \frac{4\pi k}{\lambda}$$

Fig. IV

TEA (TCNQ)$_2$
Parallel Reflectance
T = 16°K

R

Energy (eV)

965 · IBM · 01

Figure V

Figure V

Fig. VI

SOLUTION SPECTRA

TCNQ⁻	(TCNQ⁻)₂	TCNQ⁰	TTF⁺	MMP⁺
1.41				
1.63				
3.04				
	1.94			
		3.18		
			2.98	
				3.2-4.1

REFLECTANCE SPECTRA

	TCNQ⁰	Cs₂(TCNQ)₃	TEA(TCNQ)₂	TTF(TCNQ)	MMP(TCNQ)
		$1.3_\parallel$	$1.25_\parallel$	$1.22_\parallel$	$1.22_\parallel$
			$1.45_\parallel$	$1.42_\parallel$	$1.42_\parallel$
		3.0	3.0	3.0	3.0
		$2.0_\perp$	$2.0_\perp$	$2.0_\perp$	$2.0_\perp$
	$3.9_\perp$	$3.6_\perp$	$3.7_\perp$		
				$3.0_\perp$	$3.6_\perp$
C.T.		$1.0_\parallel$	$.8_\parallel$	$.9_\parallel$	$.8_\parallel$

REFERENCES FOR SOLUTION SPECTRA

TCNQ⁰, TCNQ⁻--Jonkman and Kommandeur, Chem Phys Lett, Vol 15, no. 4, pg. 496.

(TCNQ⁻)₂--Boyd and Phillips, Jour of Chem Phys, Vol 43, no. 9, pg. 2927.

TTF⁺--Hunig et al., Liebig Ann Chem, 1973, pg. 310-323.
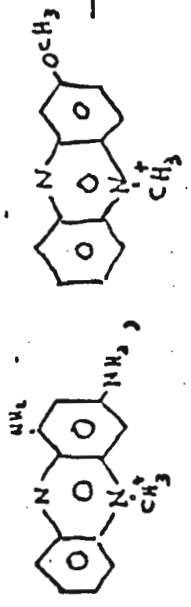
-- Absorption Spectra in UV and Visible Region