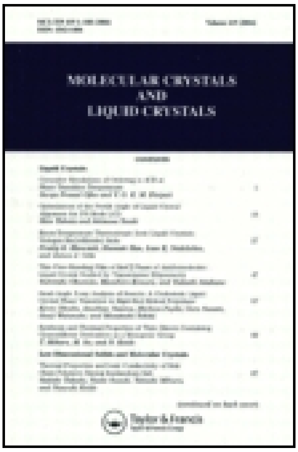

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

Analysis and Interpretation of the Reflectance Spectra of BEDT-TTF Based Charge-Transfer Salts (Organic Super-conductors and Conductors)

John R. Ferraro [a] & Jack M. Williams [a]
[a] Chemistry and Materials Science Divisions, Argonne National Laboratory, Argonne, IL, 60439, U.S.A.

Version of record first published: 22 Sep 2006.

To cite this article: John R. Ferraro & Jack M. Williams (1990): Analysis and Interpretation of the Reflectance Spectra of BEDT-TTF Based Charge-Transfer Salts (Organic Super-conductors and Conductors), Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 181:1, 253-267

To link to this article: http://dx.doi.org/10.1080/00268949008036009

Mol. Cryst. Liq. Cryst., 1990, vol. 181, pp. 253–267
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Printed in the United States of America

ANALYSIS AND INTERPRETATION OF THE REFLECTANCE SPECTRA OF BEDT-TTF BASED CHARGE-TRANSFER SALTS (ORGANIC SUPERCONDUCTORS AND CONDUCTORS)

JOHN R. FERRARO AND JACK M. WILLIAMS
Chemistry and Materials Science Divisions, Argonne National Laboratory,
Argonne, IL 60439 U.S.A.

Abstract Polarized micro-reflectance spectra of BEDT-TTF (ET) based charge-transfer (CT) superconductors and conductors are analyzed and interpreted. The paper discusses results which have allowed us to differentiate between various structural phases for $(ET)_2X$ type salts, obtain information concerning the nature of the environment in the important structure-determining anion-hydrogen cavity of these salts, and in identifying impurities present in the salts. Possible relationships of the -C-C-H bending frequency to the electronegativity of the halogen atom in the anion- hydrogen cavity and to lattice softness are cited.

INTRODUCTION

Polarized reflectance spectra for the study of charge-transfer (CT) superconductors and conductors has proven to be very useful.[1-35] Considerable information can be obtained from the spectra of these materials such as: optical anisotropy of the salts, electronic structure, plasma frequencies, optical band gap, optical conductivity, electron-phonon coupling constants and the "dimensionality" of the salt. Recent results have demonstrated that differentiation of various structural phases in $(ET)_2X$ type of salts, where ET = bis(ethylenedithio)tetrathiafulvalene, and X = inorganic anion, is also possible.[17,30] Information concerning the nature of the environments in the important structure-determining anion-hydrogen cavity of these salts can also be obtained,[17,24,29,30] as well as identifying minor impurities in these salts.[33]

Considerable data has now accumulated and it is the purpose of this contribution to examine the polarized reflectance spectra of the CT salts, and to cite the important features observed.

RESULTS AND DISCUSSION

Reflectance measurements for most CT salts have extended into the near ultraviolet region (~30,000 cm^{-1}) of the electromagnetic spectrum, and in some cases have been accomplished at liquid He temperatures. Our studies were conducted at room temperature.

The room temperature spectra of these salts are characterized by two regions of interest. The first feature is broad and extends from 4000-1600 cm^{-1} in our studies,[17,30] although the high-energy side may well extend into the high-frequency region. This feature has been ascribed to inter- and intramolecular electronic transitions of the donor molecules and their overlap, and has been designated as the plasma spectrum.[7,13] The second feature occurs from 1200-1450 cm^{-1} and has been termed the vibronic region. The emphasis in this paper deals with this latter region. The region has been attributed to the interaction between conduction electrons and molecular vibrations. The interactions involve the intramolecular, symmetric Raman-active vibrational modes of ET (e.g., A_g modes such as the C=C and C-S stretching vibrations).[7,13] It now appears the the -C-C-H bending vibrations of the ethylene groups of ET are also involved in this region, inasmuch as deuterated ET salts show changes in the vibronic region.[23,24,29-31] Coupling of the electrons with vibrational modes lowers the symmetry of the ET molecule stacks, and the vibrational spectrum becomes IR-active. A shift to lower frequency is also observed.[7,13,29] Whereas the C=C stretching vibration occurs at ~1500 cm^{-1} in the unoxidized ET molecule, the vibronic region in the salts occurs in the 1200-1450 cm^{-1} frequency range, a behavior typical of this type of phenomenon.

a. Vibronic Envelope (1200-1450 cm^{-1})

Five types of reflectance spectra are observed for the CT salts:[17,24,30]

1. Lack of envelope in this region [e.g. α-$(ET)_2I_3$ or α-$(ET)_2IBr_2$][17] - no vibrational structure observed in Fig. 1a.
2. Envelope with superimposed vibrational structure [e.g., $(ET)_2Ag_x(NCS)_2$, where x = 1.6)[34] - no dip in absorption] - Fig. 1b.
3. No envelope and only a vibrational spectrum obtained [e.g., (BEDSe-TTF)$_2$AuI$_2$), where BEDSe-TTF = bis(ethylenediseleno)tetrathiafulvalene].[32] The spectrum here is typical of an organic compound and not of an electrical conductor - Fig. 1c.
4. Envelope with no dip [e.g., deuterated ET salts,[23,24,29-31] psuedo-κ-(MDT-TTF)$_2$AuI$_2$ where MDT = (methylenedithio)tetrathiafulvalene[34] - Fig. 1d.
5. Envelope with a dip* in absorption occurring [e.g., β-, β'-, α'-, ET salts, and most PT (bis(propylenedithio)tetrathiafulvalene) salts][17] and κ-$(ET)_2Cu(NCS)_2$[24] - Fig. 1e.

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*In this paper we use the terminology of dip, which is synonymous with the splitting that occurs in the region.

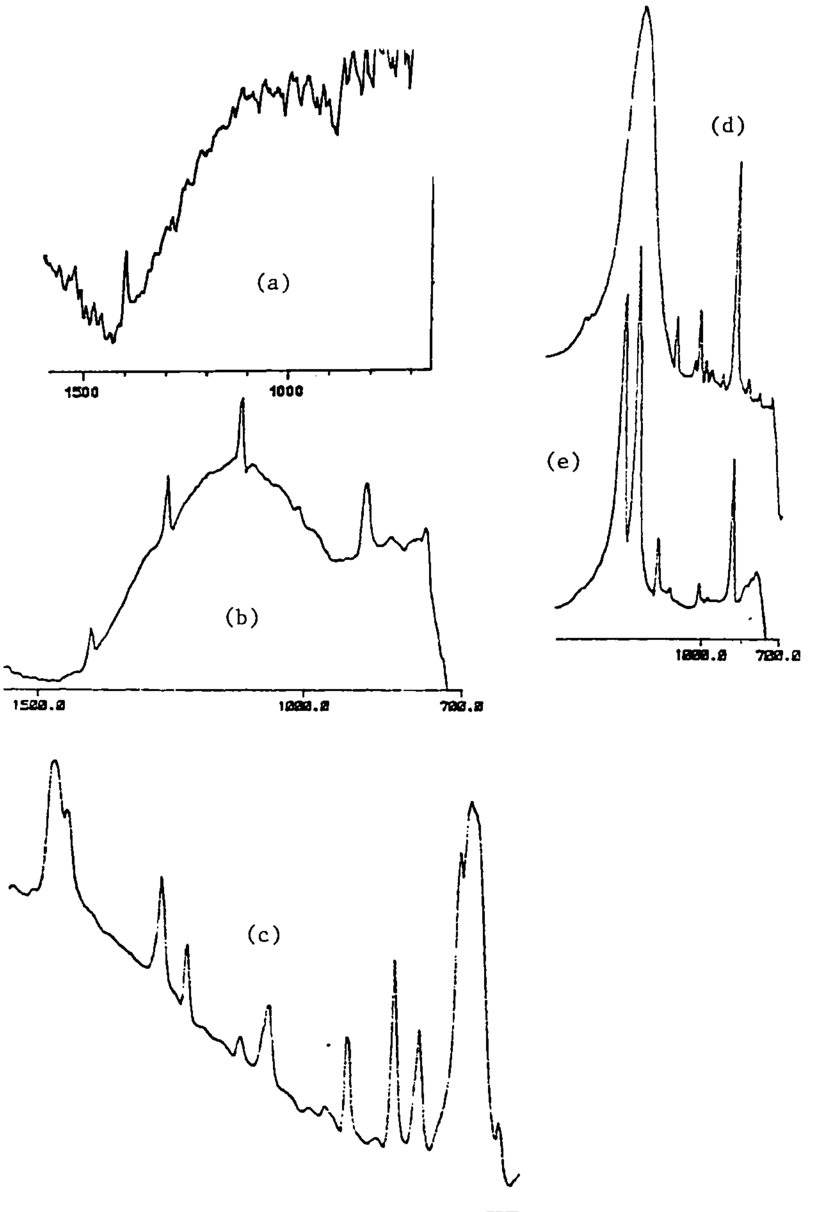


FIGURE 1 Five types of spectra obtained from reflectance studies of CT organic salts in the vibronic region:

(a) Spectrum of α-$(ET)_2IBr_2$
(b) Spectrum of $(ET)_2Ag_x(NCS)_2$, where x = 1.6
(c) Spectrum of $(BEDSe)_2AuI_2$
(d) Spectrum of κ-$d_8(ET)_2Cu(NCS)_2$
(f) Spectrum of κ-$(ET)_2Cu(NCS)_2$

The envelope may shift depending on the salt. Figure 2 illustrates this with

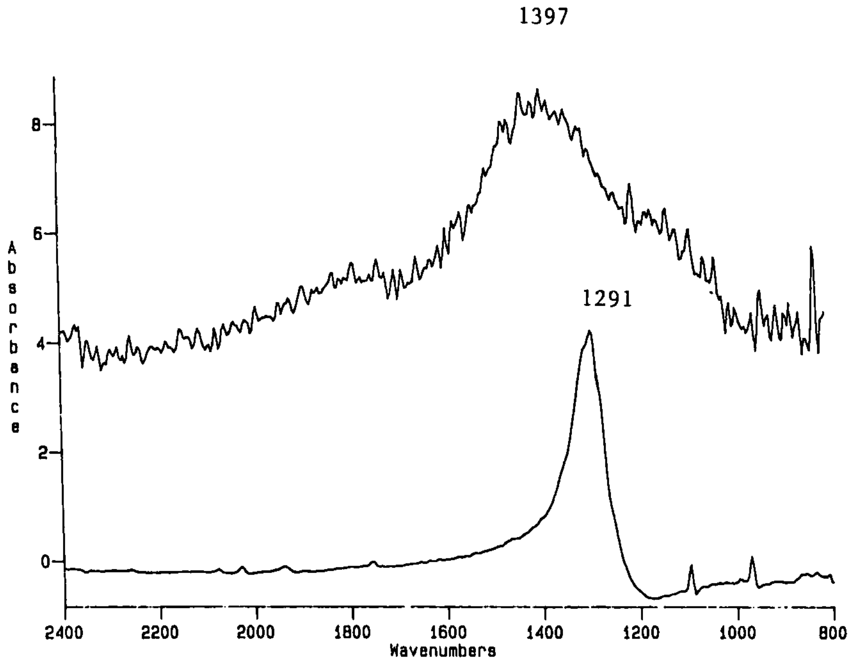


FIGURE 2 Shift in vibronic envelope (MDT-TTF)$_2$AuI$_2$ (lower), (MDT-TTF)$_2$I$_3$ (upper).

(MDT-TTF)$_2$AuI$_2$[34] where the center of the envelope is at 1291 cm^{-1} and is found close to 1400 cm^{-1} in (MDT-TTF)$_2$I$_3$.[34] The center of the envelope in (ET)$_5$Hg$_3$Br$_{11}$ is also shifted and the main peak is found at ~1400 cm^{-1}(see Fig. 3)[34] A small dip occurs at ~1300 cm^{-1} but an unsymmetrical shaped envelope makes the assignment difficult. Figure 4 illustrates the two possible shapes of the vibronic region which show dips. One is rather symmetrical, as in (ET)$_2$Au(CN)$_2$(Br)$_2$[34] and the other is asymmetric as in (ET)$_5$Hg$_3$Br$_{11}$.[34]

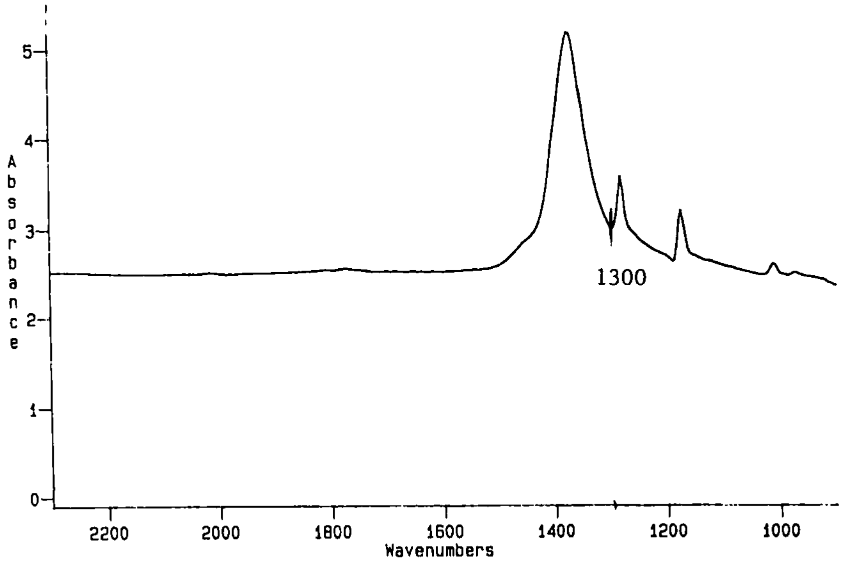


FIGURE 3 Reflectance spectra of $(ET)_5Hg_3Br_{11}$.

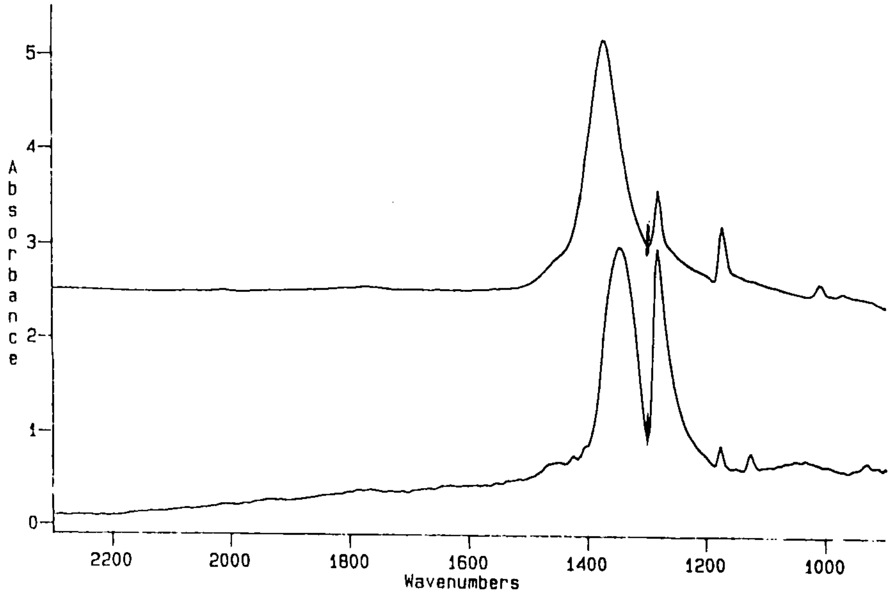


FIGURE 4 Reflectance spectra of $(ET)_5Hg_3Br_{11}$ (upper) and $(ET)_2Au(CN)_2(Br)_2$ (lower).

b. Nature of Dip in Vibronic Envelope

The dip occurring in the vibronic envelope appears to be deuterium-dependent because upon deuteration of ET salts the dip disappears.[23,23,29-31] This behavior can be attributed to the interaction of the -C-C-H bending vibration with the anion moiety. In ET salts an anion cavity exists (see Figure 5) where weak hydrogen bonding interactions between donor molecules and the anions take place, which are extremely important to the conductive properties of these materials because they are important in determining the actual solid state structures. Thus, the presence of the dip in this region is a probe of the interactions occurring in the anion cavity of these salts between the -C-C-H•••anion, involving the δ-C-C-H vibration.

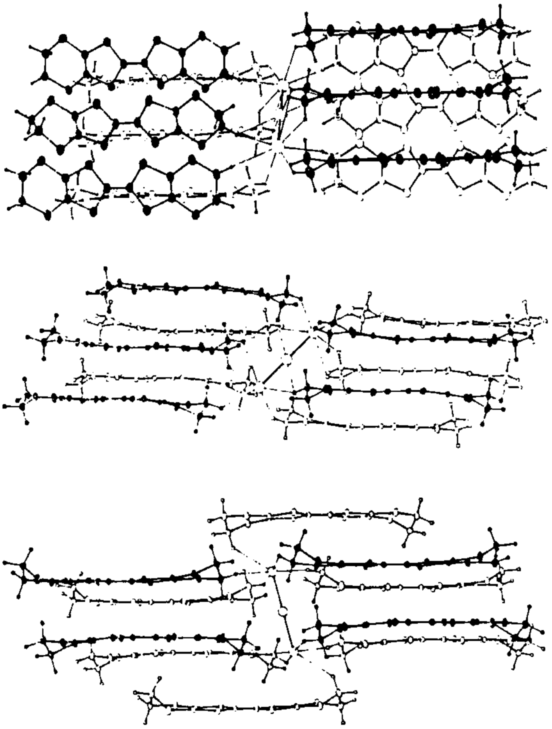


FIGURE 5 Packing diagrams for ET molecules in an environment of trihalide anions. Top: α-$(ET)_2I_3$; Middle: β-$(ET)_2IBr_2$; Bottom: β'-$(ET)_2ICl_2$.

The dip also appears to be dependent on the structural types of the salt.[17] For example, β-, β'-, α'-salts as well as κ-$(ET)_2Cu(NCS)_2$ all manifest the dip; α-structures do not. Therefore, some differentiation between structural phases is possible by the observation of the vibronic region in the reflective spectra. The dip does not appear to involve the skeletal portion of the donor molecule, as salts containing S or Se show a dip. Some of the PT salts show the dip as well (e.g., $(PT)_2I_3$, $(PT)_2IBr_2$, $(PT)_2ICl_2$, whereas the MT salts do not. The PT salts contain the -C-C-H linkage as in ET salts, whereas such a linkage is absent in the MT salts. Likewise in $(MDT\text{-}TTF)_2AuI_2$, only the vinyl and methylene linkages are present, and the salt shows no dip in the vibronic region. In the structure of $(MDT\text{-}TTF)_2AuI_2$ dimers of the donor molecules are found, and the donor molecule alternates in the dimers so that a methylene group resides over a vinyl group. Thus, each end of the molecular stack unit has only four hydrogen atoms, as compared to eight in the $\kappa\text{-}(ET)_2Cu(NCS)_2$ dimers, suggesting that fewer C-H•••anion interactions occur in the cavities of MDT-TTF and MT salts.

c. Identification of Two Orientations of ET Molecules in $\kappa\text{-}(ET)_2Cu(NCS)_2$ by Reflectance Methods

Examination of the vibronic region from polarizing reflectance studies has also been found to be useful in identifying two different ET molecules in the highest-T_c organic superconductor known (T_c = 10.4K) $\kappa\text{-}(ET)_2Cu(NCS)_2$.[24] It was found that the frequency differences occur in the δ-C-C-H vibration for the two molecule types in $\kappa\text{-}(ET)_2Cu(NCS)_2$. One form shows the δ-C-C-H vibration at 1280 cm^{-1} and the other at 1302 cm^{-1}. Figure 6 illustrates the IR reflectance spectra of $\kappa\text{-}(ET)_2Cu(NCS)_2$.

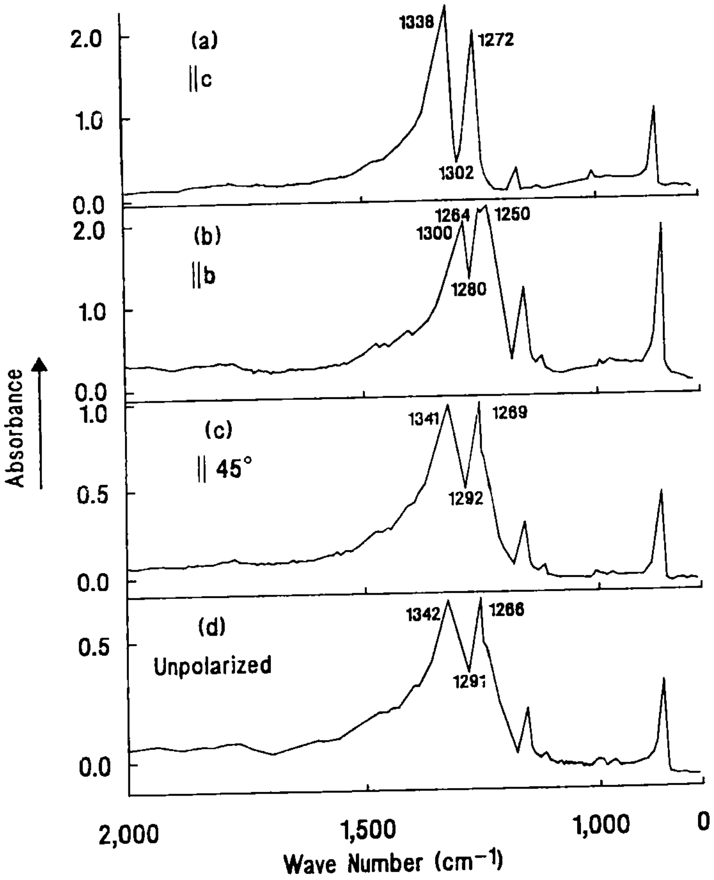
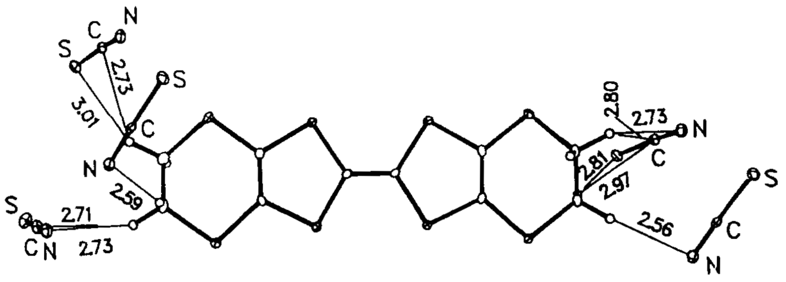
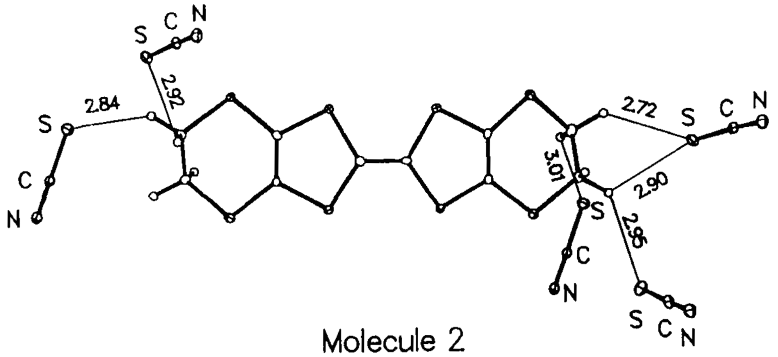


FIGURE 6 Polarized reflectance spectra of κ-(ET)$_2$Cu(NCS)$_2$.

(a) polarized light parallel to c-axis,
(b) polarized light parallel to b-axis,
(c) polarized light parallel to 45° between b and c axis and
(d) unpolarized light.



Molecule 1



Molecule 2

FIGURE 7 Two types of ET molecules in $(ET)_2Cu(NCS)_2$ and their SCN^- environment. Thin lines are short H•••anion contacts less than the van der Waals radii sum (3.1 Å, 3.0 Å and 2.85 Å for H•••S, H•••C and H•••N, respectively.

Figure 7 shows the two types of ET molecules in κ-$(ET)_2Cu(NCS)_2$ and their (SCN^-) anion environments. The results substantiate the x-ray data for this salt, where the independent ET molecules exist in the unit cell.[36] The short C-H•••anion contacts are associated with the two non-equivalent ET molecules (Fig. 7). Molecule 1 has short C-H•••anion contacts primarily with the N and C atoms, whereas molecule 2 has short C-H•••anion contacts primarily with the S atoms. The two environments lead to two different -C-C-H bending modes in the polarized infrared reflectance spectra of κ-$(ET)_2Cu(NCS)_2$.[24]

d. Possible Relationship Between the δ-C-C-H Frequency Dip and the Electronegativity of the Halogen Atom in the Anion Cavity

The position of the δ-C-C-H frequency (dip) in the reflectance spectra may be related to the electronegativity of the halogen atom in the cavity.[17] For PT salts, the δ-C-C-H frequency shifts toward higher energy as the electronegativity of the halogen atoms of the anion increases. For example, in the anions involving PT as a donor, the δ-C-C-H frequency shifts toward higher energy in the order of $I_3^- \rightarrow I_2Br^- \rightarrow ICl_2^-$ indicative of stronger hydrogen bonding occurring in the cavity of the salt, as the electronegativity of the halogen atom increases. Additional work is necessary to further substantiate any possible trend.

e. Possible Correlation of δ-C-C-H Bending Frequency with the Lattice Softness

Correlation of the bending frequency with "lattice softness" may also be possible.[17] Whangbo, et al.[37] have correlated the H•••H and H•••X bond lengths in the hydrogen-anion cavities of ET salts with the "softness" of ET molecule-anion interactions (softness being defined as soft in respect to phonon modes such as translational or librational). When the lattice of the ET salts is soft toward phonon modes, it leads to a large electron-phonon coupling constant (λ). The constant increases as the lattice becomes softer and T_c increases. This follows from the McMillan equation[38]

$$T_c = (\theta_D/1.45)\exp[-1.04(1 + \lambda)/(\lambda-\mu^* 1 + \lambda<\omega>/\omega_o)] \qquad (1)$$

where θ_D is the Debye temperature in a given lattice, $<\omega>$ and ω_0 are the average and the maximum frequencies of the phonon band, respectively, μ^* is the Coulomb psuedo potential. Based on the BCS mechanism[39] of superconductivity, the electron-phonon coupling is essential for superconductivity. The extent of coupling is measured by the constant λ, which is related to T_c as in equation 1. Using observed T_c values for the β-$(ET)_2X$ series, and $\mu^* = 0.1$, $<\omega>/w_0 = 0.3$ and $\theta_D = 200$ K, one obtains the values in Table I. The superconductor β^*-$(ET)_2I_3$ refers to the phase obtained if β-$(ET)_2I_3$ is pressed at pressures > 0.5 kbar. It follows that λ increases as T_c increases and a "softening" of the lattice occurs. Figure 8 illustrates the difference between the staggered and eclipsed configuration of ET molecules listed in Table I.

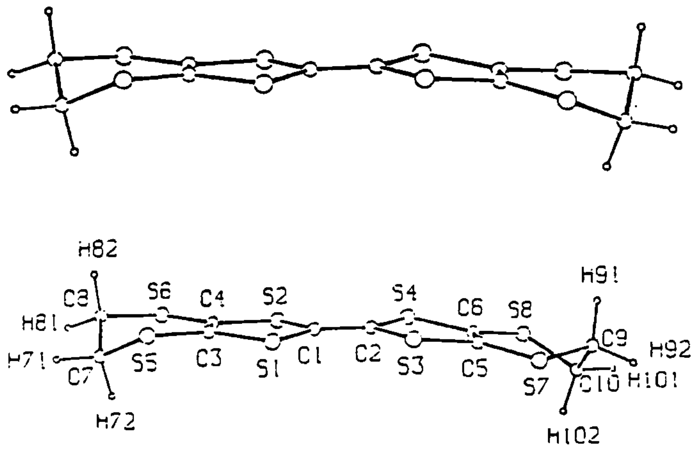


FIGURE 8 Staggered (bottom) and eclipsed (top) ET molecules.

TABLE I

Salt	T_c (K)	λ	ET molecule arrangement	H•••X$^-$ (A)	H•••H (A)
β-(ET)$_2$I$_3$	1.4	0.37	eclipsed	2.842	2.477
			staggered	2.988	2.152
β-(ET)$_2$IBr$_2$	2.8	0.43	eclipsed	2.887	2.169
β-(ET)$_2$AuI$_2$	5.0	0.52	eclipsed	2.996	2.224
β*-(ET)$_2$I$_3$	8	0.62	staggered	3.014	2.261

Superconducting Transition Temperature (T_c)
Electron-Phonon Coupling Constant (λ)
Conformation of ET molecule, H•••X$^-$, H•••H
Bond Distances in β-(ET)$_2$X Salts

In the PT salts studied[17] the δ-C-C-H vibrations occur 5-10 cm^{-1} lower than in the ET salts, indicative of slightly stronger hydrogen-anion interactions in the cavity (decrease in softness) for the ET salts vs. the PT salts. With an increase in H•••X$^-$ distances (see

Table I) the υ_{CH} stretching frequencies should increase and δ-C-C-H frequencies should decrease within the ET series seen in Table I. Unfortunately, the insensitivity of the δ-C-C-H vibration in the ET series prevents one from determining if this suggestion is valid. The broad plasma band in the higher region masks the CH stretching vibrations. Additional problems in quantifying such an effect are based on the fact that as yet there are an insufficient number of members within a series to examine, and also that the possibility that structural differences can occur within the series.

f. Identification of Minor Impurities

The microreflectance IR technique has also proven useful in identifying minor impurities in various organic CT salts. In the thermal conversion of semiconductor α-$(ET)_2I_3$ to the superconductor α_t-$(ET)_2I_3$, some evidence for slight decomposition is noticed in the thermal tempering reaction.[33] A red spot in the α_t-$(ET)_2I_3$ sample was identified by the microreflectance technique to have absorptions that could be assigned to neutral ET (red-orange color).[31]

EXPERIMENTAL

ET salt analyses were performed on a BioRad FTS-40 Micro-IR instrument. A narrow-band MCT detector with a 250μm diameter element was mounted on the UMA-300A microscope. The single crystal was placed on a KBr salt plate to eliminate any reflection/absorption effects from the sample mount. The salts are opaque and the spectra were measured in the reflectance mode. The typical microscope aperture was set to produce a 220μm square sampling area. A sputtered gold plate was substituted for the sample to obtain an instrument background. The spectra for the 4000-700 cm^{-1} region were acquired at 4 cm^{-1} resolution for either 30 or 500 seconds of scanning time. A Kramers/Kronig transformation was applied to all microreflectance spectra and added 40 seconds to the analysis time. Infrared microsampling has become a powerful analytical tool for the characterization of very small samples (> 5μm).

SUMMARY

The analysis and interpretation of the micro-reflectance spectra of BEDT-TTF based salts has been made. Two main features of the spectra are found. The first feature from 4000-1600 cm^{-1} is attributed to the plasma spectrum extending from higher energy and involving inter- and intramolecular electronic transitions of the donor molecules and their overlap. The second feature occurs from 1200-1450 cm^{-1} and is the vibronic region and is attributed to interaction between conduction electrons and molecular vibrations and to the anion-hydrogen interactions in the cavity of these salts. The latter feature appears to be the fingerprint of these interactions occurring in the anion-hydrogen cavity between donor and anions, which are very important to the structural and physical properties in these materials.

The micro-reflectance infrared region has also been shown to be useful in differentiating between various structural-types in $(ET)_2X$ salts. The β-, β'-, α'- and κ-$(ET)_2Cu(SCN)_2$ salts all show spectra of the type illustrated in Fig. 1e (where a dip in absorption occurs in the vibronic region), whereas α-structures show no dip (Fig. 1a).

The technique is also useful in detecting impurities in these salts.

Acknowledgments:

The authors wish to acknowledge the assistance of M. A. Beno, K. D. Carlson, A. M. Kini, U. Geiser, A. J. Schultz and H. H. Wang of Argonne National Laboratory, to S. Hill and K. Krishnan of Bio-Rad, Digilab Division, Cambridge, MA, and to M.-H. Whangbo of North Carolina State University for valuable discussions. This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Material Sciences under Contract W-31-109-ENG-38.

REFERENCES

1. H. Tajima, K. Yakushi, H. Kuroda, G. Saito, and H. Inokuchi, Solid State Commun., 49, 769 (1984).
2. C. S. Jacobsen, Ib. Johannsen and K. Bechgaard, Phys. Rev. Lett., 53, 194 (1984).
3. H. Tajima, K. Yakushi, H. Kuroda and G. Saito, Solid State Commun., 56, 251 (1985).
4. B. Koch, H. P. Geserich, W. Ruppel, D. Schweitzer, K. H. Dietz and H. J. Keller, Mol. Liq. Mol. Cryst., 119, 343 (1985).
5. H. Tajima, K. Yakushi, H. Kuroda and G. Saito, Solid State Commun., 56, 159 (1985).
6. T. Sugano, K. Yamada, G. Saito and M. Kinoshita, Solid State Commun., 55, 137 (1985).
7. M. G. Kaplunov, E. B. Yagubskii, L. P. Rosenberg and Y. G. Borodko, Phys. Stat. Sol. (a), 89, 509 (1985).
8. H. Kuroda, K. Yakushi, H. Tajima and G. Saito, Mol. Cryst. Liq. Cryst., 125, 135 (1985).

10. T. Sugano and G. Saito, J. Phys. C. Sol. St. Phys., 19, 5471 (1986).
11. H. Tajima, H. Kanbara, K. Yakushi and G. Saito, Solid State Commun., 57, 911 (1986).
12. C. S. Jacobsen, J. Phys. C. Sol. St. Phys., 19, 5643 (1986).
13. M. Meneghetti, R. Bozio and C. Pecile, J. Physique, 47, 1377 (1986).
14. A. Ugawa, K. Yakushi, H. Kuroda, A. Kawamoto and J. Tanaka, Chem. Lett., 1875 (1986).
15. K. Yakushi, H. Kanbara, H. Tajima, H. Kuroda, G. Saito and T. Mori, Bull. Chem. Soc. Jpn., 60, 4251 (1987).
16. C. S. Jacobsen, D. B. Tanner, J. M. Williams, U. Geiser and H. H. Wang, Phys. Rev. B, 35, 9605 (1987).
17. J. R. Ferraro, H. H. Wang, J. Ryan and J. M. Williams, Appl. Spectrosc., 41, 1377 (1987).
18. M. G. Kaplunov, R. N. Lyubovskaya, M. Z. Aldoshima, Yu C. Borodko, Phys. Stat. Sol. (a), 104, 833 (1987).
19. A. Ugawa, K. Yakushi, H. Kuroda, A. Kawamoto and J. Tanaka, Synth. Met., 22, 305 (1988).
20. K. Yukushi, H. Tajima, T. Ida, M. Tamura, H. Hayashi, H. Kuroda, H. Kobayashi and R. Kato, Synth. Met., 24, 301 (1988).
21. M. Yoshitake, K. Yakushi, H. Kuroda, A. Kobayashi, R. Kato and H. Kobayashi, Bull. Chem. Soc. Jpn., 61, 1115 (1988).
22. A. Ugawa, G. Ojima, K. Yakushi and H. Kuroda, Synth. Met., 27, A445 (1988).
23. M. Tokumoto, H. Anzai, K. Takahashi, N. Kinoshita, K. Murata, T. Ishiguro, Y. Tanaka, Y. Hayakawa, H. Nagamori and K. Nagasaka, Synth. Met., 27, A171 (1988).
24. J. R. Ferraro, H. H. Wang, U. Geiser, A. M. Kini, M. A. Beno, J. M. Williams, S. Hill, M.-H. Whangbo and M. Evain, Solid State Commun., 68, 917 (1988).
25. H. Kuroda, K. Yakushi, H. Tajima, A. Ugawa, M. Tamura, Y. Okawa and A. Kobayashi, Synth. Met., 27, A491 (1988).
26. F. L. Pratt, W. Hayes, M. Kurmoo and P. Day, Synth. Met., 27, A439 (1988).
27. A. Ugawa, G. Ojima, K. Yakushi and H. Kuroda, Phys. Rev. B, 38, 5122 (1988).
28. M. Tamura, K. Yakushi, H. Kuroda, A. Kobayashi, R. Kato and H. Kobayashi, J. Phys. Soc. Jpn., 57, 3239 (1988).
29. T. Sugano, H. Hayashi, H. Takenouchi, K. Nishikida, H. Urayama, H. Yamochi, G. Saito and M. Kinoshita, Phys. Rev., 37, 11387 (1988).

30. J. R. Ferraro and J. M. Williams in, "FT-IR Spectroscopy in Industrial and Laboratory Analyses" J. R. Ferraro and K. Krishnan, Eds., Academic Press, San Diego, CA (1989).

31. H. H. Wang, P. E. Reed and J. M. Williams, Synth. Met., 14, 165 (1986).

32. H. H. Wang, L. K. Montgomery, U. Geiser, L. C. Porter, K. D. Carlson, J. R. Ferraro, J. M. Williams, M. Evain, J. J. Novoa and M.-H. Whangbo, Chem. of Materials, 1, 140 (1989).

33. H. H. Wang, J. R. Ferraro, K. D. Carlson, L. K. Montgomery, U. Geiser, J. R. Whitworth, J. A. Schlueter, S. Hill, M.-H. Whangbo, M. Evain and J. A. Novoa, Inorg. Chem., 28, 2267 (1989).

34. J. R. Ferraro, unpublished data.

35. T. Sugano, H. Hayashi, M. Kimoshita and K. Nishikida, Phys. Rev. B, 39, 11387 (1989).

36. H. Urayama, H. Yamochi, G. Saito, S. Sato, A. Kawamoto, J. Tanaka, T. Mori, Y. Maruyama and H. Inokuchi, Chem. Lett., 463 (1988).

37. M.-H. Whangbo, J. M. Williams, A. J. Schultz, T. J. Emge and M. A. Beno, J. Am. Chem. Soc., 109, 90 (1987).

38. W. L. McMillan, Phys. Rev., 167, 331 (1968).

39. J. Bardeen, L. N. Cooper and J. R. Schrieffer, Phys. Rev., 106, 162 (1957); 108, 1175 (1957).