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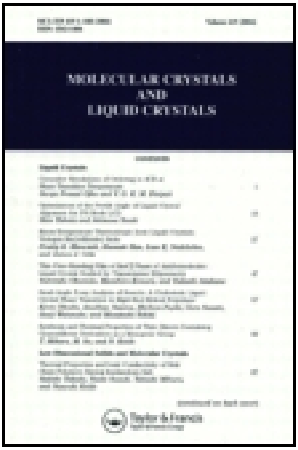

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Infrared and Raman Study of the Anion-Donor Interactions in Tetrahedral Anion $(TMTSF)_2$ X and $(Tmttf)_2$ X Salts

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INFRARED AND RAMAN STUDY OF THE ANION-DONOR INTERACTIONS IN TETRAHEDRAL ANION $(TMTSF)_2X$ AND $(TMTTF)_2X$ SALTS

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Abstract Some spectral features that can be used to probe the anion-donor interactions have been identified in the infrared absorption spectra of the title compounds with $X=ReO_4^-$, BF_4^-, and ClO_4^-. The sudden increase of vibronic absorption intensities observed at the anion ordering (AO) transitions in the ReO_4^- and BF_4^- salts of TMTSF and TMTTF shows that the ordering is accompanied by a distortion of the conducting chains. An anomalously large splitting is observed for these salts at low temperature in the 1500-1650 cm^{-1} region where the ring C=C stretching modes are expected to occur. However a single resonance is observed for the central C=C stretching mode in the Raman spectra. Analysis of the spectroscopic data point to a strong intramolecular polarization of the electronic charge on the TMTSF or TMTTF units induced by the interaction with the anions. The localization of carriers along the chains is either much less than predicted by the theory or its effects are averaged by rapid random motions of the carriers. Neither the stack distortion nor the charge polarization are observed in $(TMTSF)_2ClO_4$ below the AO transition.

INTRODUCTION

Soon after the discovery of the Bechgaard phases it was realized that their behavior, unusual if compared with that of previously

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known quasi-1D conductors, might be related to the presence of relatively strong interchain coupling along the b direction and of the commensurate potential of the anion sublattice.[1] Nowadays, while the applicability of 1D physics to this class of compounds at low temperature is still a matter of controversy, the relevance of the anion-donor interactions is widely recognized.[2] The anion sublattice induces a small dimerization gap in the electronic spectrum of the TMTSF chains and therefore introduces umklapp scattering in these compounds. In the context of g-ology models, much attention has been paid to the effects of this type of processes in determining the phase diagram of the $(TMTSF)_2X$ systems.[1,2] In salts with tetrahedral anions the consequences of the anion-donor interactions are most dramatic since the ordering of the anion sublattice at relatively high temperatures may drive the system into an insulating CDW state.[1,2]

Infrared spectroscopy in the intramolecular vibrational region is now established as a powerful tool for investigating the electronic and structural properties of quasi-1D conductors and in particular for monitoring the onset of CDW and periodic lattice distortions of the conducting chains.[3] Furthermore, the well documented sensitivity of the vibrational spectra to a wide range of crystal interactions makes IR and Raman spectroscopy a technique of choice for an investigation of the anion-donor interactions and of their effect on the structure of the TMTSF molecules. The present IR and Raman work aims at a comparative study of the effects of the anion-donor interactions in both $(TMTSF)_2X$ and $(TMTTF)_2X$ salts with the tetrahedral anions $X=ReO_4^-$, BF_4^-, and ClO_4^-. The results of this study allows us to gain some insight into the nature of the anion-cation interaction and to test the hypothesis[4] of a charge localization below the anion ordering (AO) transition in $(TMTSF)_2ReO_4$ and other materials.

EXPERIMENTAL

Single crystals of the (2:1) salts of TMTSF and TMTTF were prepared by the standard electrochemical method. The instrumentation and procedures used in obtaining the powder absorption spectra were as previously reported.[3,5] The Raman spectra were excited by the 476.2 nm line of a Kr^+ ion laser and dispersed by a Spex double monochromator. Single crystals of the

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salts were aligned on the tip of a Cryodyne cryocooler and the laser beam was focussed onto them by a cylindrical lens.

RESULTS AND DISCUSSION

With reference to the powder absorption spectra of $(TMTSF)_2ReO_4$ shown in Fig.1, let us first identify the changes which occur in the intramolecular vibrational features upon going through the 180K anion ordering (AO) transition and that turn out to be useful in characterizing the anion-donor interactions. Most noteworthy is

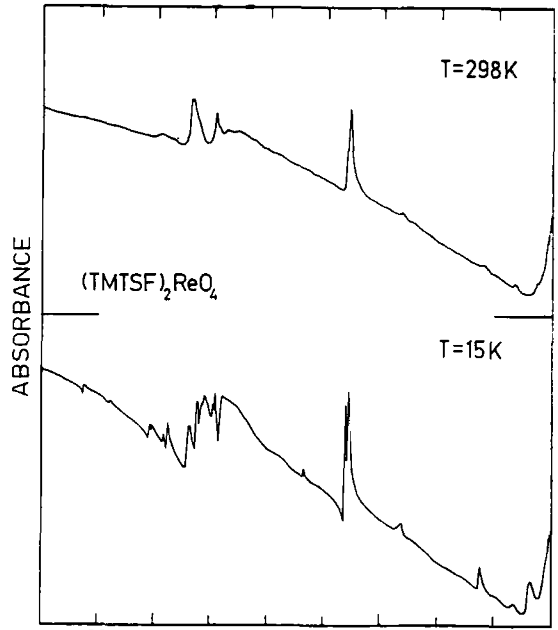

FIGURE 1 Infrared absorption spectra of $(TMTSF)_2ReO_4$ powders at T = 298 K and T = 15 K.

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the growth of a broad asymmetric feature around 1400 cm^{-1} accompanied by that of less prominent and narrower bands at 440 and 265 cm^{-1}. These spectral features have been discussed in a previous work by ourselves [5] and subsequently by Jacobsen et al.[6] They are originated by the coupling of conduction electrons to intramolecular vibrations, namely, the totally symmetric (a_g) modes ν_4, ν_9, and ν_{10} respectively. Note that their appearancce in the spectra is a signature of a periodic distortion of the conducting chains.[3,5]

The results of a detailed comparative study of these temperature dependent vibronic absorptions in tetrahedral anion salts of TMTSF and TMTTF will be reported in a forthcoming paper. They may be summarized as follows. (i) The sudden increase of the vibronic absorption intensities at the AO transitions in the (2:1) TMTSF and TMTTF salts with ReO_4^- and BF_4^- demonstrates that the transitions in all these systems have a displacive character in that the anion ordering is accompanied by a distortion of the organic chains. (ii) No such effect is observed in the perchlorate salts irrespective of the different symmetry of the anion ordering in the TMTSF and in the TMTTF salt ((a, 2b, c) and (2a, 2b, 2c) respectively). (iii) The large vibronic intensities observed above the AO transition temperatures for the TMTTF salts, in contrast to the TMTSF ones, indicates a greater tendency of the sulphur compounds to undergo a dimeric distortion induced by the interaction with the anions. This might be explained by the presence of larger electron-electron correlations [5,7] or by a stronger one-dimensionality or, more likely, by both factors.[7]

In this paper we shall mainly focus on another type of temperature dependent spectral feature, namely, an anomalously large splitting of normally infrared active modes observed in the range from 1500 to 1650 cm^{-1}. For the case of $(TMTSF)_2ReO_4$ this effect can already be seen in the spectra of Fig.1. Details of the spectral region and of its temperature evolution are shown in Fig.2 for all the TMTSF and TMTTF salts studied in this work.

One can see that, although different in the spectral details, the splittings displayed by both perrhenate salts (Fig.2a and 2d) are of comparable magnitude. Note that the observed value of about 50 cm^{-1} is far beyond that expected for ordinary Davydov excitonic splittings. A similar effect, although again different in the details, is observed for the fluoroborate salt of TMTSF but not for that of TMTTF. Conversely, none of the two perchlorate salts display such a splitting.

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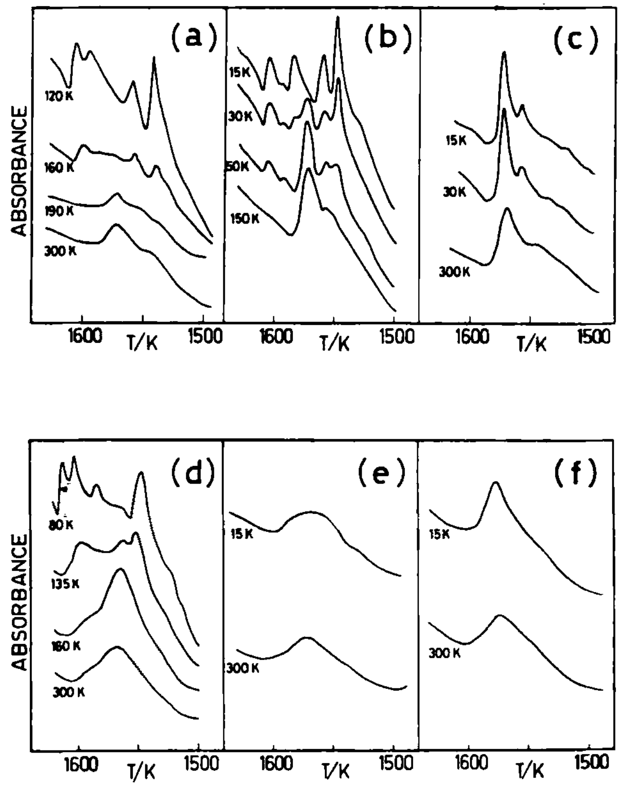

FIGURE 2 Temperature dependence of the 1500-1650 cm^{-1} spectral region of (TMTSF)$_2$X (upper) and (TMTTF)$_2$X (lower) salts with X=ReO$_4^-$: (a) and (d); BF$_4$: (b) and (e); ClO$_4^-$: (c) and (f).

The relation of the observed splittings to the occurrence of the AO transitions is clearly seen in Fig.3 where the observed peak frequencies are plotted against temperature for all the cases in which the splitting is observed. One can see that the spectral changes occur critically at the phase transition temperatures indicated by arrows in the Figure.

In the frequency region of interest only one fundamental ungerade mode is expected to occur for both TMTSF and TMTTF namely the $\nu_{28}(b_{1u})$ mode.[8] The atomic displacement vectors of this mode

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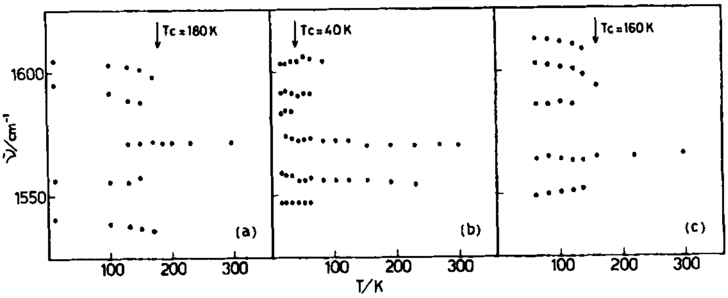

FIGURE 3 Observed frequencies vs. T for (a) $(TMTSF)_2ReO_4$, (b) $(TMTSF)_2BF_4$, and (c) $(TMTTF)_2ReO_4$.

are shown in Fig.5a: it corresponds to an anti-phase stretching vibration of the two ring C=C double bonds. In addition, a vibronic absorption corresponding to the totally symmetric mode a_g, ν_3 (Fig. 5b) should appear whenever a periodic distortion of the organic chain is present. Its frequency is expected to be downshifted with respect to the corresponding Raman frequency.[5,6]

The relevant frequency values (in cm^{-1}) taken from Ref.8 are given in the following:

		molecule	cation	averaged
TMTSF:	b_{1u}, ν_{28}	1617	1558	1587
	a_g, ν_3	1625	1573	1599
TMTTF:	b_{1u}, ν_{28}	1627	1547	1587
	a_g, ν_3	1639	1567	1603

Note that the averaged frequency values should be observed when the charge carriers, that is the holes, are delocalized or rapidly moving along the stacks.

The possible occurrence of combination frequencies should also be taken into account. As a matter of fact one such frequencies appears to be the origin of the shoulder at 1550 cm^{-1} in

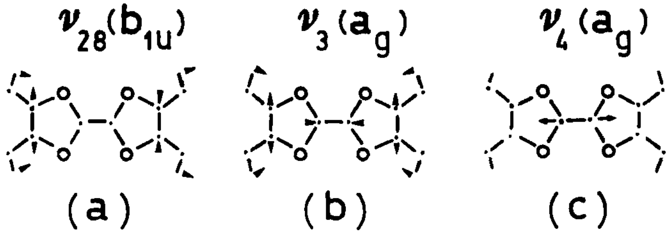

FIGURE 4 Atomic displacement vectors for the (a) b_{1u}, ν_{28}; (b) a_g, ν_3, and (c) a_g, ν_4 modes.

$(TMTSF)_2ClO_4$ which at low temperature develops into a distinct peak at 1557 cm^{-1} (Fig. 2c).

Details of the discussion leading to a vibrational assignment of the observed absorption peaks of Fig.2 and 3 will be given elsewhere. In summary, one might at first consider two possible alternative schemes. The main feature of the temperature evolution of the spectra, that is the 50 cm^{-1} splitting, may originate from the fact that, owing to the interaction with the anions, the charge carriers are effectively localized below the AO transition so that the averaging of the neutral molecule and cation radical frequencies is not anymore effective at low temperature. This would represent an experimental confirmation of the theoretical model recently proposed by Bruinsma and Emery [4] for the AO transition in $(TMTSF)_2ReO_4$. Another possible origin of the observed phenomenon might be a strong asymmetry of the intramolecular electron distribution induced by the interaction with the anions. The resulting inequivalence of the two ring C=C bonds would give rise to two infrared active frequencies instead of only one ungerade frequency (b_{1u}, ν_{28}) and one Raman-active gerade mode (a_g, ν_3).

As a mean to distinguish between these two alternatives we have considered looking at other intramolecular modes. The most suitable choice appears to be the totally symmetric Raman-active ν_4 mode (neutral molecule, cation radical, and average frequencies are: 1539, 1399, 1469 cm^{-1} for TMTSF; 1538, 1418, 1478 cm^{-1} for TMTTF).[8] It corresponds to the stretching of the central C=C bond (Fig.5b) and therefore it should display two distinct frequencies only in the case that the charges are localized on alternate molecular units.

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The Raman spectra of oriented single crystal mosaics of the perrhenate salts of TMTSF and TMTTF and of (TMTSF)$_2$BF$_4$ at 15K are shown in Fig.6. It is at first glance apparent that the hypothesis of charge localization seems to be contradicted by the Raman data since a single resonance is observed for the ν_4 mode at a frequency close to the average of the neutral and ionized molecule frequencies.

This result may be due to either of two factors: (a) the modulation of the carrier density along the stacks is not enough to split the ν_4 mode into two separate resonances or (b) incoherent random motion of the localized carriers is fast enough to motionally narrow the two resonances corresponding to mostly ionized and mostly neutral molecules. In other words, case (a) would correspond to the absence of inhomogeneous broadening of the spectral line whereas case (b) would correspond to the motional narrowing of the inhomogeinity effects. Indications against the hypothesis of case (a) come from the large value of the gap induced by the anion ordering in (TMTSF)$_2$ReO$_4$.[2] The degree of localization, being related to the gap amplitude, should correspondingly be non negligeable and is estimated to be on the order of a lattice spacing.[4] If case (b) applies, a lower limit for the hopping rate can be obtained by using the Kubo theory [9] of modulation narrowing for the analysis of the observed lineshapes. Assuming an essentially complete localization on alternate dimers

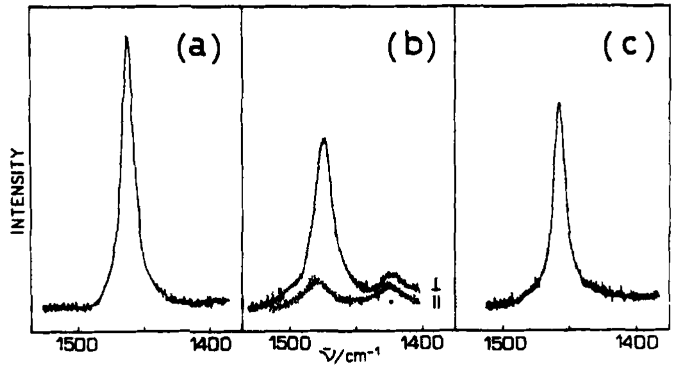

FIGURE 5 Raman spectra of (a) (TMTSF)$_2$ReO$_4$, (b) (TMTTF)$_2$ReO$_4$, and (c) (TMTSF)$_2$BF$_4$ at 15 K (nominal) in the ν_4 mode region.

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and knowing the resonance frequencies for the two inequivalent sites in the limit of zero hopping rate, that is in our case the isolated neutral molecule and radical cation, we can get an estimate of the hopping rate from a comparison of the observed and the calculated lineshapes. Actually, owing to the limited spectral resolution of the data and to the numerous other factors contributing to the lineshape, we can only have a lower limit to the hopping rate. To reproduce the observed Raman bandwidths of 10-15 cm^{-1} we need hopping rates on the order of 10^{-13}-10^{-14} s. Of course slower rates would result if one assumes a smaller degreee of localization.

In the light of this result the interpretation of the large splitting of ungerade modes observed in the infrared in terms of charge localization seems untenable. The alternative explanation that we must look for should account for the fact the phenomenon is observed only for certain salts as well as for the fact that it involves specifically the stretching of the ring C=C bonds. Note that, taking into account the results for both the TMTSF and TMTTF salts, the infrared data indicate that the strenght of the anion-donor interactions is in the order $ReO_4^- > BF_4^- >> ClO_4^-$. Consideration of the available structural data [1,2] indicates that the presence of short anion-donor contacts cannot by itself justify the different behavior of the salts. Another factor on which we have focussed our attention is the difference in electronegativity between central atom and the oxygen or fluorine atoms of the anions (Δ(electronegativity): BF_4^-, 2.09; ReO_4^-, 2.04; ClO_4^-, 0.67)[10]. This factor determines the amount of negative charge residing on the outer atoms of the anion.

The justification of the peculiar sensitivity of the ring C=C bond stretching frequencies to the intramolecular electron polarization might be given in terms of valence bond structures following the so called "spin-charge separation and charge localization" model previously introduced by Wudl.[11] The anion-donor interaction stabilizes the valence structure in which the positive charge of the TMTSF cation is on the selenium atom closest to the anion. As shown in Ref.11, in this structure the bonding of the two opposite C-C bond is different, in fact one is a single and one is a double bond. Thus, to the extent that this valence structure is stabilized compared to the others, the two vibrational frequencies are expected to split apart.

In summary, the spectroscopic data point to a strong intramolecular polarization of the electronic charge on the

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TMTSF/TMTTF units induced by the interaction with the anions. However this phenomenon is not quite general. In fact it occurs only with certain anions and only below the AO transitions. It is remarkable in this respect that $(TMTSF)_2ClO_4$, the ambient pressure organic superconductor, does not display neither the stack distortion nor the charge polarization below the AO transition.

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