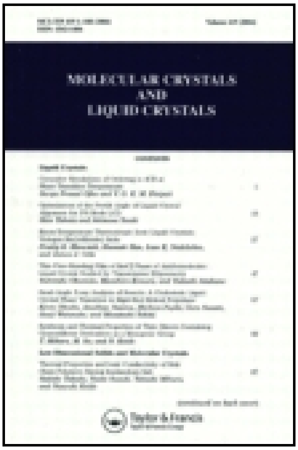

Molecular Crystals and Liquid Crystals

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Optical Properties of some TMTS(T)F_2X Compounds

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OPTICAL PROPERTIES OF SOME TMTS(T)F_2X COMPOUNDS*

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The infrared and visible reflectance of $TMTSF_2PF_6$ is reported. Data are given at high and low temperatures in the metallic range and for polarizations along and perpendicular to the highly conducting direction. Among the interesting features are a pseudogap in the far infrared conductivity along the highly conducting direction, and a mid-infrared plasma edge in the perpendicular direction. Unusual temperature dependent, near infrared absorptions may have implications for the band structure. For comparison some data on $TMTSF_2AsF_6$, $TMTSF_2ClO_4$, $TMTSF_2ReO_4$ and $TMTTF_2PF_6$ are presented.

INTRODUCTION

Complex 2:1 salts based on the molecules TMTSF (tetramethyltetraselenafulvalene) and TMTTF (tetramethyltetrathiaful-

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valene) combined with various inorganic anions are of great current interest. These isomorphous materials exhibit a number of fascinating physical properties, including low temperature metallic behavior[1], as well as superconducting[2], antiferromagnetic[1], Peierls[3], and order-disorder transitions[3].

In the present work we have used infrared and optical spectroscopy to achieve an overall picture of the excitation spectra of $TMTSF_2PF_6$ as function of temperature in the metallic phase. For comparison we have in addition obtained selected data on other materials in the series.

EXPERIMENTAL

The measurements were done on single crystals of typical dimensions 5×0.7×0.3 mm^3. The morphology is such that the crystals are elongated along the chain direction or crystallographic a-axis. The largest optical faces are in the a-b plane. The direction perpendicular to a in this plane is called b'. The stacks of organic molecules form sheets in the a-b planes with anion layers in between. The third direction, c, is roughly normal to the sheets.[4]

Single crystal polarized reflectance data were taken

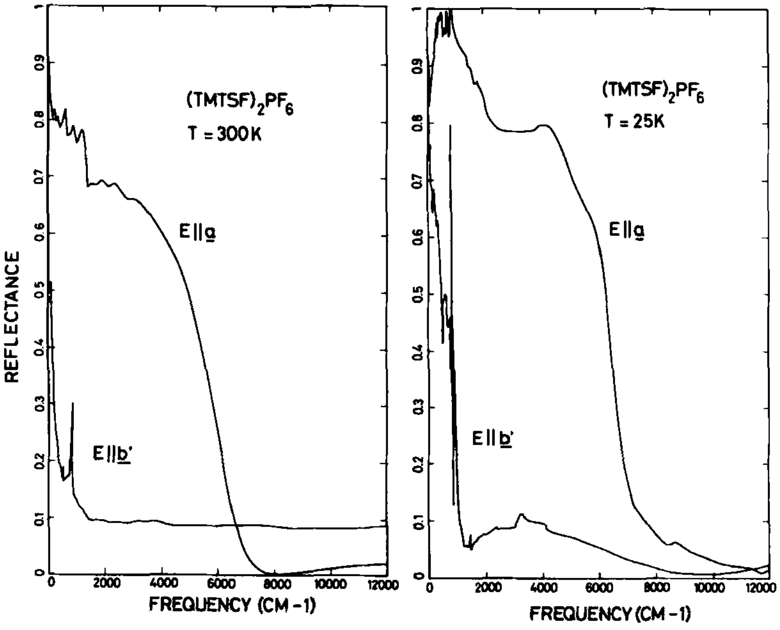

FIGURE 1 Polarized reflectance of $TMTSF_2PF_6$ at (a) 300K and (b) 25K.

over the frequency range 10-25.000 cm^{-1}. Single beam dispersive spectrometers were used in the mid-infrared through visible. The far infrared measurements were done on a Michelson interferometer. The sample for the far infrared was an assembly of optically aligned crystals.

The sample temperature was varied by anchoring the crystal mount to a controlled cold finger.

RESULTS AND DISCUSSION

In Fig 1(a) and (b) we show the infrared reflectance of $TMTSF_2PF_6$ polarized along a and b' at T = 300K and T = 25K respectively. The essential new feature, when compared to the reflectance spectra of other quasi-one-dimensional conductors, is the rise of a plasma edge in the perpendicular polarization, b', at low temperature. This feature has been taken as evidence for $TMTSF_2PF_6$ being effectively two-dimensional at low temperature[5]. While this transverse plasma edge is situated near 1000 cm^{-1}, the edge for E||a is close

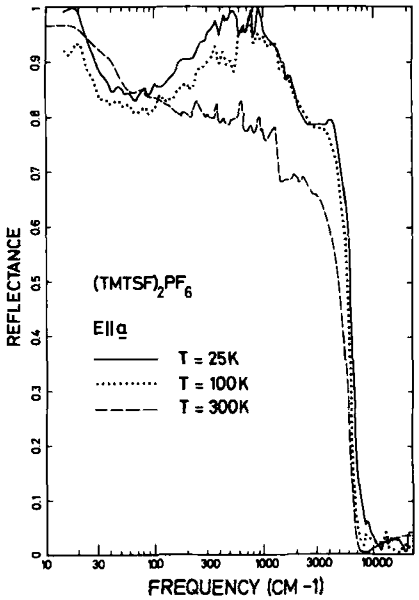

FIGURE 2 Chain axis reflectance of $TMTSF_2PF_6$ at various temperatures. Note the logarithmic frequency scale.

to 7000 cm^{-1} and quite similar to that of other organic conductors. Using a simple Drude model for the reflectance components and a tight-binding band structure, the positions of the plasma edges correspond to tight-binding transfer integrals of 250 meV and 3 meV for $\underline{a}$ and $\underline{b}$ respectively[5]. These numbers are clearly crude estimates since the reflectance spectra, especially at low temperatures, are not quite Drude like. The main deviations observed are for $E\|\underline{a}$: The minimum in the far infrared (below 300 cm^{-1}), the drop-off in the 1000-2000 cm^{-1} range, and the apparent smearing of the plasma minimum at 8000-10000 cm^{-1}. For $E\|\underline{b}'$ a broad minimum appears around 10000 cm^{-1} at low temperature. The strong line near 840 cm^{-1} is easier to explain. It originates from the strong vibrational absorption in the PF_6^--ion[6].

In the following we will discuss in more detail the implication of these non-Drude like features.

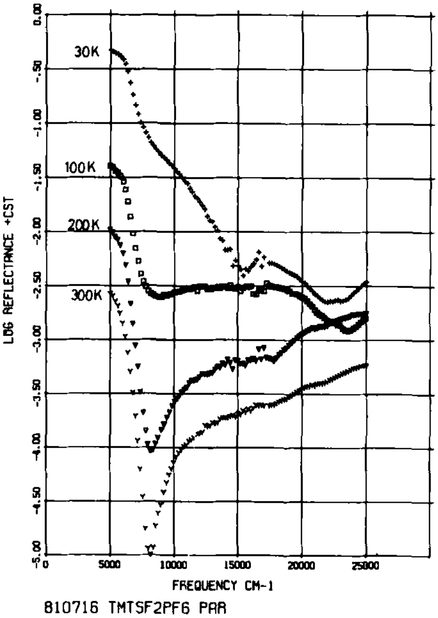

FIGURE 3 Chain axis reflectance of $TMTSF_2PF_6$ at various temperatures. Note the logarithmic reflectance scale. The curves are arbitrarily displaced in the vertical direction.

Chain Axis Data

Starting with the chain axis polarization we show in Fig. 2 the temperature dependence of the reflectance, R, from 15-20000 cm^{-1}. At all temperatures R heads toward unity at the lowest frequencies as appropriate for a conductor. This observation gives confidence in the experimental data. Going up in frequency a very clear minimum develops with decreasing temperature, centered around 50 cm^{-1} and extending from 20-300 cm^{-1}. In the range 300-1000 cm^{-1} the average reflectance level goes from around 80% to just a few percent below 100% on cooling. Above 1000 cm^{-1} R falls again. A rather rapid fall is observed near 1300 cm^{-1} at T = 300K. At low temperature the fall is more gradual, extending to above 2000 cm^{-1}. These latter features may be attributed to the effects of coupling between the conduction electron and the intramolecular vibrations in the TMTSF-molecules[7]. The final complicating feature, i.e. the smearing of the plasma minimum is more clearly seen in Fig. 3, which shows R on a logarithmic scale at various temperatures and in the near infrared to visible. From 300K to

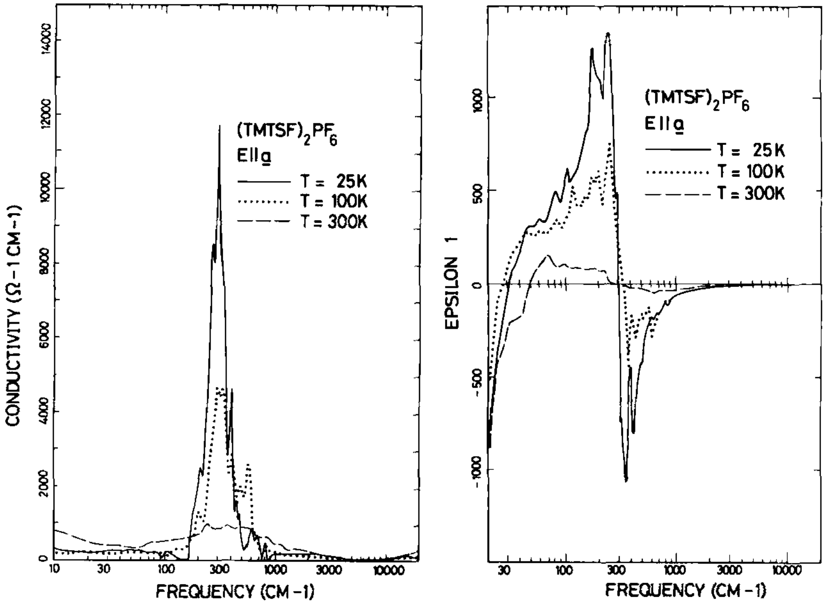

FIGURE 4 (a) Frequency dependent conductivity and (b) dielectric function of $TMTSF_2PF_6$ as obtained from chain axis reflectance. Notice the logarithmic frequency scales.

200K the depth of the minimum decreases by a factor of 2. At 100K the minimum has all but gone and at 30K a broad shoulder has appeared. The origin of this effect is clearly a gradual growth of extra absorption around 10000 cm^{-1}. We offer two possible explanations for this absorption. First, the weak dimerisation of the chains[4] should introduce a small optical absorption around 4t~1eV (t is the transfer integral). The absorption increases quadratically with the dimerisation gap. Thus an increase in dimerisation on cooling could give an effect as observed. The second possibility involves electron correlation effects. In that case the optical absorption near 1eV should crudely correspond to a charge transfer excitation involving double occupancy[8]. However, it seems difficult to account for the temperature dependence in such a picture.

We now return to discuss the low frequency range. The data of Fig. 2 have been analyzed by the Kramers-Kronig transformation[9] to give the frequency dependent conductivity and dielectric function, which are shown in Fig. 4 (a) and (b).

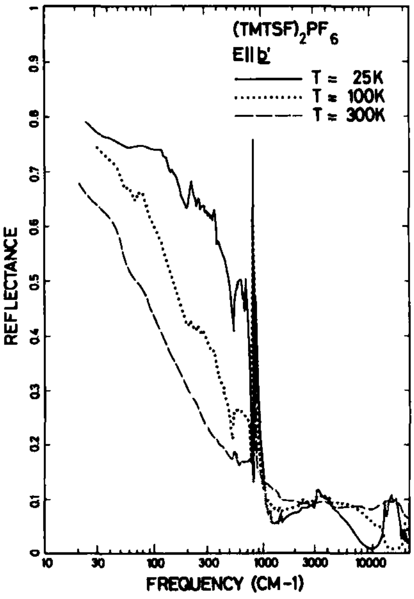

FIGURE 5 b-axis reflectance of TMTSF$_2$PF$_6$ at various temperatures. Note the logarithmic frequency scale.

It is evident that the low far infrared reflectance corresponds to a rather low far infrared conductivity: Almost all the intraband oscillator strength is contained in the peak centered at 300-400 cm^{-1}. The width of the peak is about 200 cm^{-1} at 25K, but increases to about 1500 cm^{-1} at 300K. The low far infrared conductivity is remarkable in view of the reported DC and microwave conductivity (σ_{DC} = 2-5×10^4 $\Omega^{-1}cm^{-1}$ at T = 25K[10]). The 300 K conductivity extrapolates quite well to the correct DC value. In contrast, the frequency dependent conductivity at low temperatures must contain a very sharp, almost delta function like, contribution at zero frequency. The oscillator strength of this contribution can be estimated from the reflectance or from the dielectric function, ε_1 (Fig. 4(b)). As R→1 for ω→0, ε_1 is rolling off to high negative values. Thus the data directly indicates the existence of the sharp zero frequency mode. A least squares fitting to the measured reflectances indicates a strength in the mode of order 1-2% of the strength in the 300 cm^{-1} peak. The reflectance in the measured range is quite insensitive to

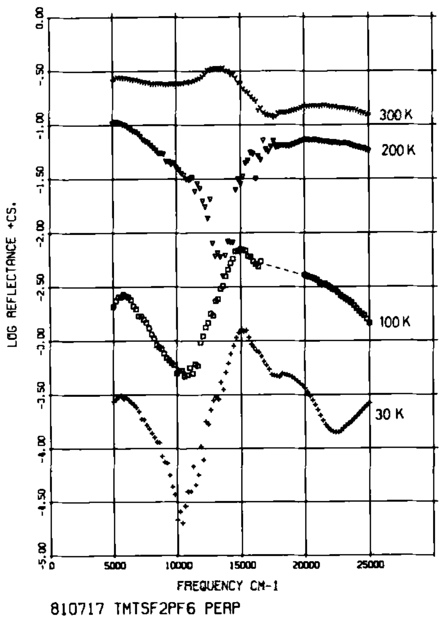

FIGURE 6 b-axis reflectance of $TMTSF_2PF_6$ at various temperatures. Note the logarithmic reflectance scale. The curves are arbitrarily displaced in the vertical direction.

the width of the narrow mode, which therefore only can be determined indirectly from the known DC-conductivity.

Presently we can offer no explanation for the anomalous far infrared properties.

Data for Other Directions

The temperature dependence of the b'-axis reflectance is shown in Fig. 5. Here it is quite evident how the gradual rise in R as $\omega \to 0$ at 300K (corresponding to an overdamped plasmon), sharpens up to a well-defined edge with an associated minimum at 1200 cm^{-1} at low temperature. Superimposed are various vibrational lines. As mentioned above, the growth of the edge is not the only temperature dependent feature. The development of the new near-infrared absorption is more clearly seen in Fig. 6, which shows the near infrared to visible, temperature dependent reflectance on a logarithmic scale. The 300K spectrum shows one resonance near 15000 cm^{-1}, which tentatively is identified as the lowest internal excitation in the $TMTSF^{o}/TMTSF^{-}$ molecules.

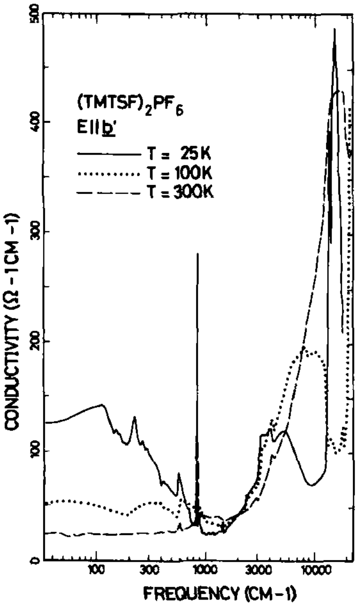

FIGURE 7 Frequency dependent conductivity of $TMTSF_2PF_6$ along b' as obtained from reflectance. Note the logarithmic frequency scale.

At 200K a remarkable change has occurred: a sharp minimum near 13000 cm^{-1} has developed. On cooling this minimum is shifted to lower frequencies.

A Kramers-Kronig transformation of the data in Fig. 5 is presented in Fig. 7 as the frequency dependent conductivity. The new low temperature absorption band is centered around 5000 cm^{-1}. The temperature dependence of the line suggests that it is very sensitive to the thermal contraction, e.g. interatomic distances. Thus it is conceivable that important changes in the band structure take place on cooling. Another possible interpretation again involves correlation effects: the absorption could be a temperature dependent charge transfer band corresponding to an onsite Coulomb repulsion.

Fig. 7 also shows the intraband Drude contribution (below 2000 cm^{-1}). At 25K it is reasonably well-defined and apart from vibrational structure it is quite Drude like. The extrapolated zero frequency value is somewhat higher than the measured σ_{DC}^{11}, which, however, is not very accurately determined.

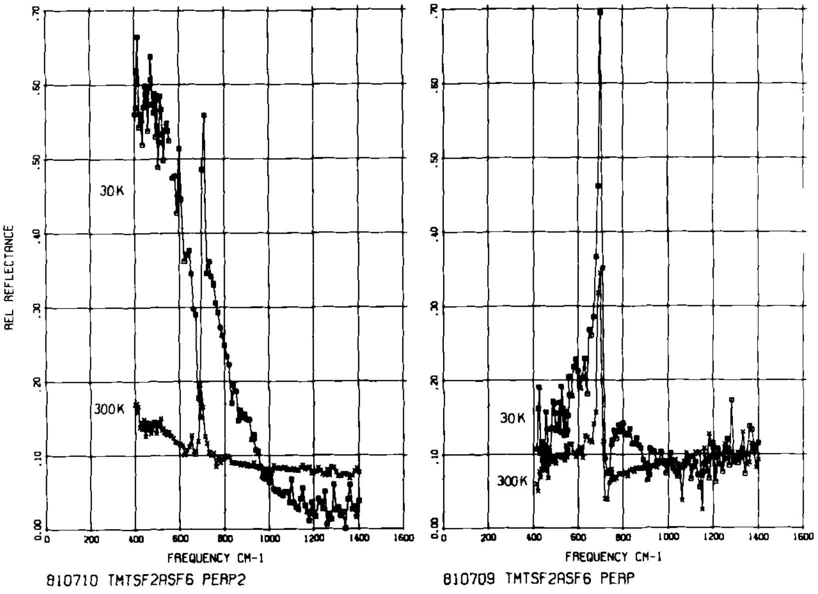

FIGURE 8 Polarized reflectance of TMTSF$_2$AsF$_6$ for (a) $E||\underline{b}'$ and (b) $E||\sim\underline{c}$ at 300K and 30K.

In order to verify the interpretation of the 1000 cm^{-1} edge in reflectance as a metallic plasma edge, we have repeated the measurement on other materials. As expected, the structure is absent in the non-conducting low temperature states of TMTSF$_2$ReO$_4$ and TMTTF$_2$PF$_6$ (see also below).

Fig. 8(a) and (b) show on a linear scale the b' and ~c reflectance components in TMTSF$_2$AsF$_6$ at 300K and 30K. This material is quite similar to the PF$_6$-compound, but it is available in larger crystals, thus making the third direction accessible for optical experiments. As expected, the behavior along b' is quite similar to that of TMTSF$_2$PF$_6$, E||b', while the ~c polarization merely shows a strong AsF$_6^-$ band near 700 cm^{-1}.

Fig. 9 presents similar data for TMTSF$_2$ClO$_4$, which is of special interest because it has a superconducting ground state at ambient pressure[12]. Part of the explanation for that could be the smaller interchain distances found here[12]. The resultant larger contact along b should show as a blue shift of the plasma edge. No such effect is evident from Fig. 9 (as compared to Fig. 8(a)). However, a detailed fit which takes into account the vibrational bands, suggest a

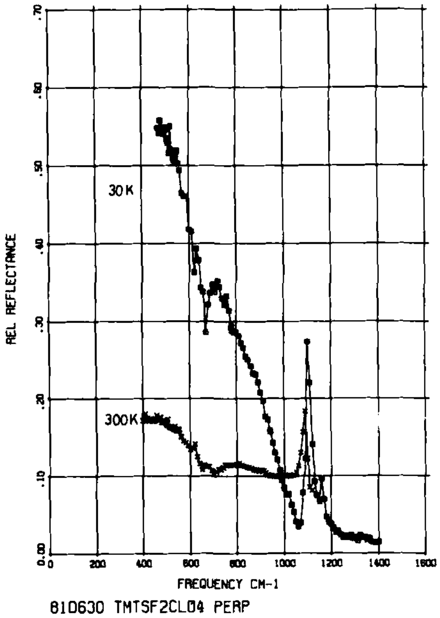

FIGURE 9 Polarized reflectance of TMTSF$_2$ClO$_4$ for E||b' at 300K and 30K.

~15% increase in transverse plasma frequency going from the AsF_6^- to the ClO_4^- compound. The corresponding increase in $t_\perp$ would be approximately 30%, which is a sizable effect.

Semiconducting Materials

It is instructive to compare the chain axis excitation spectra of $TMTSF_2PF_6$ and other materials in the series with qualitatively different electronic properties.

In Fig. 10(a) and (b) we show the frequency dependent midinfrared conductivity of $TMTSF_2ReO_4$ at 300K and 40K. In this material a 3D ordering of the ReO_4^- ions provokes a sharp transition at 183K from a conducting to a semiconducting state[1,3]. Already at room temperature (Fig. 10(a)) the vibrational structure is stronger than in $TMTSF_2PF_6$ and the conductivity peak is centered around 1000 cm^{-1}. Below the transition (Fig. 10(b)) the picture has drastically changed. A clear gap in the continuum has appeared at ~1500 cm^{-1} in reasonable agreement with the value deduced from the DC conductivity activation energy (~1400 cm^{-1})[13]. The very

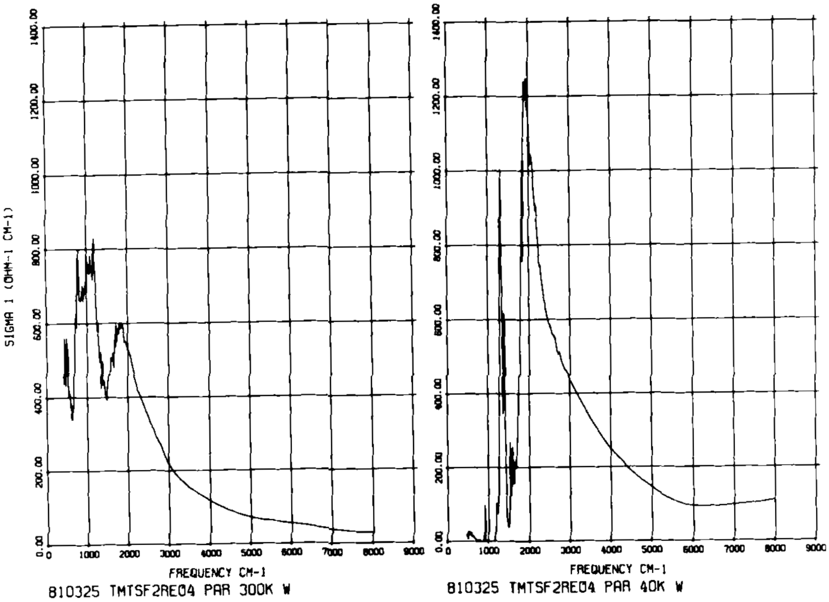

FIGURE 10 Frequency dependent conductivity of $TMTSF_2ReO_4$ at (a) 300K and (b) 30K as obtained from chain axis reflectance.

strong absorption lines below the gap originate from the electron-molecular-vibration coupling and contains information on coupling constants etc.[14]. Note that the strong line near 1300 cm^{-1} shows up as a broad indentation in the 300K spectrum.

The final example is given in Fig. 11. Here is shown the frequency dependent conductivity at 300K of $TMTTF_2PF_6$, $E \| a$. This material is basically semiconducting with $\sigma_{DC}(300K) \sim 20 (\Omega^{-1}cm^{-1})$[15]. The low conductivity is thought to be due to the band being narrow as compared to the on-site Coulomb repulsion. Correspondingly the infrared spectrum shows the intraband oscillator strength centered around 2200 cm^{-1}. On the low energy side the effect of the vibrational coupling is again clear.

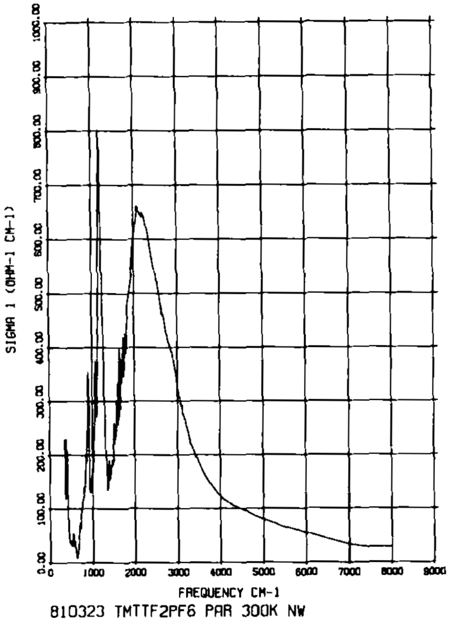

FIGURE 11 Frequency dependent conductivity of $TMTTF_2PF_6$ at 300K as obtained from chain axis reflectance.

CONCLUSIONS

We briefly summarize the results and the implications:

1. The existence of a transverse plasma edge in the sheets of TMTSF stacks is well established. The position of the edge does not change drastically from material to material. No edge is found along c. Thus the conducting TMTSF$_2$X materials can be described as anisotropic quasi-twodimensional metals at low temperature.
2. The distribution of oscillator strength along the chains is highly anomalous at low temperature. The pseudo gap in the far infrared must be explained by a proper theory. A similar feature was observed in TTF-TCNQ[16], but has there been explained in terms of charge density wave formation. No charge density waves have been seen in TMTSF$_2$PF$_6$ [3].
3. Temperature dependent near infrared absorptions have been observed. These could indicate qualitative changes in band structure with temperature. Supplementary work is needed for clarification.
4. Comparative studies on isostructural, conducting as well as semiconducting materials should prove useful in gaining understanding of the effects of electron-phonon coupling, Coulomb correlation effects, and over-all band structure.

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