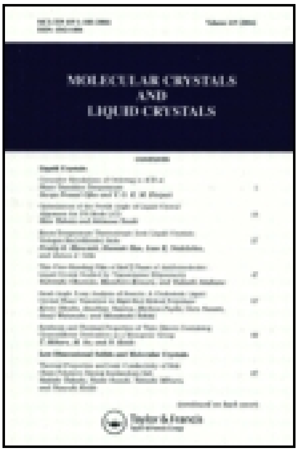

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SPECTRAL STUDY OF NEW ORGANIC CONDUCTORS DERIVED FROM A GIANT ANALOGUE OF TTF

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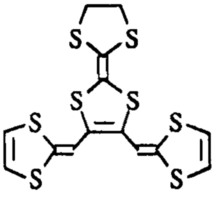
Abstract. Infrared absorption spectra of salts derived from a new giant analogue of TTF (D) with small inorganic anions have been measured *vs* temperature. Spectra of the neutral donor (D) and compounds used in its building were studied also. A comparative analysis was used for assignment of the fundamental vibrations of D and its cation-radical salts. Shape of the spectra, i.e. linewidthes and intensities of selected bands, appearance of CT bands above 4000 cm^{-1} etc., suggest a 1:1 stoichiometry of the salts. T-dependencies of intensities of some bands of $DClO_4$ and $DCu(SCN)_2$ show anomalies which reveal the presence of phase transitions. Observed anomalies are preliminary explained.

INTRODUCTION

Since the discovery of the first organic metal TTF-TCNQ,[1] attention has been focused on strong electron donor or acceptor molecules as potential basic structures to produce synthetic metals or organic superconductors. Among the electron donors, a cardinal role is held by TTF which has generated many families of organic conductors. Subtle chemical modifications of the TTF framework[2] have allowed to change their physical properties. One of the present trend lies in the building of sulphur rich analogues of TTF.[3] We have focused on a giant analogue of TTF in which the dihydro-TTF core is bearing two conjugated 1,4-dithiafulven-6-yl side arms:

D



Infrared spectroscopy can contribute significantly to investigation of the physical properties of the cation-radical salt of D with small inorganic anions. Their stucture based on giant molecular units makes the study of the role of molecular vibrations very informative.The aim of this work is to obtain informations on eventual phase transitions from temperature variations of intramolecular vibrations; an attribution of the main bands and evaluation of the salts stoichiometry will be discussed also.

EXPERIMENTAL

The donor molecule synthesis and its electrochemical oxidation in the corresponding charge transfer salts have been reported previously.[3,4] The cation-radical salts of D with such anions as PF_6^-, ClO_4^-, $Cu(SCN)_2^-$ or $H_2F_3^-$ have been obtained as quite small needle-shaped crystals or black powders. The infrared absorption spectra were studied on polycristalline samples suspended in KBr host. IR spectra of the salts, neutral D and compounds used in its building, were measured in the range 600-4000 cm^{-1} using a PERKIN ELMER spectrometer model 841, at temperatures ranging from 85 to 300 K. Raman spectra of the donor were recorded with 1.06 μm laser excitation.

RESULTS AND DISCUSSION

The donor molecule (its crystallographic data are not available) can be referred to the point group C_2. Thus fundamental modes (90 normal vibrations) are of A or B symmetry. Assuming a planar skeleton, its symmetry can be C_{2v}, and even in this case the normal vibrations of the symmetry A_1, A_2, B_1 and B_2 are only possible. It means that totally symmetric A_g modes, of fundamental importance for establishing of an electron-molecular vibration coupling, are absent in the donor molecule.

At present it is not possible to give a complete assignment of all fundamental vibrations of D. Thus we have carried out a tentative assignment using correlations between its spectra and those for compounds containing D fragments or used in the building of this donor. The frequencies of the strongest IR and Raman bands and their assignment are collected in Table I (the observed intensities of the bands are marked using universally known abbreviations). UV-VIS spectrum of D in CH_2Cl_2 contains the electron excitation bands at 20 400 cm^{-1}, 21 280 cm^{-1}, 25 640 cm^{-1}, 29 610 cm^{-1} and 40 000 cm^{-1}.

IR spectra of the ion-radical salts of D with small anions PF_6^-, ClO_4^-, $Cu(SCN)_2^-$ or $H_2F_3^-$ are, in general, superpositions of a charge transfer (CT) band, the strongest bands of the donor (deplaced and deformed as usual) and the bands of inorganic anions (marked

TABLE I IR and Raman spectra of donor and derived salts.

Donor			Ion-radical salts			
Frequencies (cm^{-1})						
IR	Raman	Assignment	DPF$_6$	DClO$_4$	DCu(SCN)$_2$	DH$_2$F$_3$
3063 m	3090 3062	sym. and asym. CH stretch.				
2913 w		CH$_2$ stretch.				
					2090	
1826 vw						
1633 vw						
1547 vs	1546	C=C stretch. (ring)	1505	1468	1463	1495 1474
1514 vs	1508	C=C stretch. (centr.)	1464	1455	1431	1432
1468 w		CH$_2$ scissor.				
1442 w	1445					
1415 m		sym. CH$_2$ wagg.	1384	1368	1384	1372
1380 w						
	1325					
1294 vs		CH$_2$ wagg.+ CH$_2$ twist.				
1273 vs		CH$_2$ wagg.+ CH$_2$ twist.	1276	1276	1273	
1240 m	1250	CCH bend.+ CH wagg.	1255	1239	1232	1238
1141 m		CCH bend.	1153	1147	1147	1148
1128s	1130	CCH bend.	1120	1120	1120	1125
1104 m	1102					**1095**
1083 m		CCH bend.		**1082**	1090	**1030**
993 m		CS strech. + CCS bend.(ext.)				992
973 m						
917 m						
899 m						
869 w		SCS deformation				
848 s		asym. SCS+ CS bend. + CH$_2$ rock.	**842**		848	848
802 vs		SCC bend.(ring) + CS stretch.	800	795	785	784
775 vs		CS stretch.	741	745	743	739
761 vs		CS stretch.	722			
740w						
670 w	673	CH$_2$ rock.	665	664	664	665
638 w	654	sym. and asym. CCS stretch.				
633 s		CS stretch. + asym. SCS deformation		622		619
609 w						
	468					

as bold letters in Table I).A typical spectrum of the salt e.g. for $DClO_4$ (fig.1) shows the vibrational bands larger (25 $cm^{-1} < \Delta v < 90$ cm^{-1}) and more intensive than the corresponding bands of the neutral donor (5$cm^{-1} < \Delta v < 20$ cm^{-1}); the CT band is found distinctly above 4000 cm^{-1}. These spectral features confirm the 1:1 stoichiometry of the salt determinated by X-ray method.[4] In case of other stoichiometry or a partial charge transfer, the bands should be considerably broader and CT band should be situated at about 4000 cm^{-1}.[5] The spectra of the remaining three salts show the same features and a similar appearance. This is why one can settle the same 1:1 stoichiometry of the salts and similar degree of charge transfer approximate to 1. The electrical conductivity estimations[4] agree also with above conclusions.

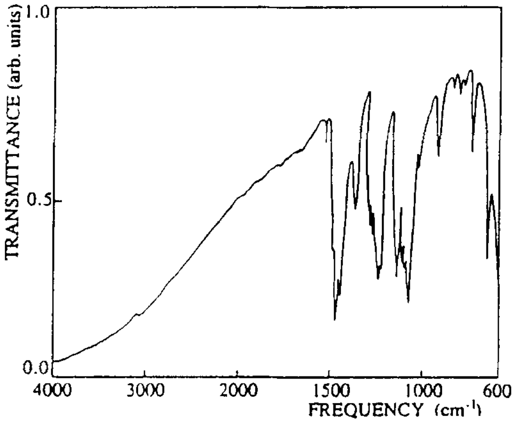


FIGURE 1 IR transmittance of $DClO_4$

The bands just below 800 cm^{-1}, assigned to C-S stretching and SCC (ring) bending are strongly weakened in the ion-radical salts of D. This reflects changes in the charge distribution at the donor molecule after formation of the salts; in particular, the spectral investigation suggests that the electron density at the sulfur atoms is strongly disturbed. This is not the case with the salt DH_2F_3, the bands of which, below 800 cm^{-1}, remaining relatively strong. It means that the interaction between $H_2F_3^-$ and $D^{+\cdot}$ is weaker than between other anions and $D^{+\cdot}$ in the remaining salts. It may suggest also a different crystal structure of DH_2F_3.

Figure 2 shows the absorption spectrum of DH_2F_3 at 83K and 293K. Little by little evolution of the spectrum with decreasing the temperature is its distinctive mark.The spectra of the three remaining salts change likewise.

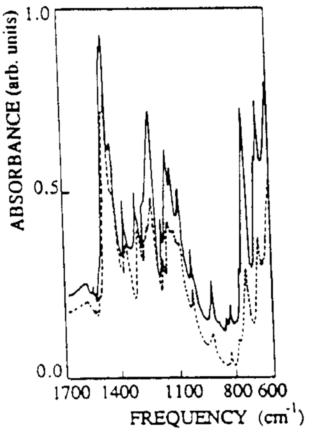


FIGURE 2 IR absorption of DH_2F_3 at 83K (full line) and 293K (dashed line)

At low temperature the bands are better separated, their intensities (I) are distingly higher and their linewidthes narrower. Exact analysis of the frequences and linewidthes *vs* temperature do not reveal any anomaly. On the contrary the T-dependences of line intensities are diverse and show some interesting features (fig. 3). These dependences for DPF_6 and DH_2F_3 salts are smoth and show only a normal T-dependency. The intensities of some bands of $DClO_4$ change suddenly at T ≈ 230K. The jump of I (T) corresponds to a broadening and a splitting of the ESR line observed at about 215K .[6] These observations prove a phase transition to happen in $DClO_4$ salt at about 220K. Another, but not so sudden increase of the band intensities is also observed at about 135K. It may be indicative of a reorganization in the electron system since ESR study do not reveal any anomaly at this T-range.The T-dependence of the IR band intensities of the $DCu(SCN)_2$ salt reveals very strong anomaly at about 140K. Some of the bands, in particular at 743 cm^{-1} and 1147 cm^{-1} (fig. 3) change their intensities nearly 5 time from high to low temperature. However the band at about 664 cm^{-1}, attributed to CH_2 rocking, increases even above 9 time. One can distinguish, except that of 664 cm^{-1}, the bands at 655 cm^{-1} and 637 cm^{-1} of medium intensities and at 617 cm^{-1} of very small intensity.These three bands disappear instantly above T = 140K . Mentioned triplet correspond to frequencies 638 cm^{-1}, 633 cm^{-1} and 609 cm^{-1} found in the spectrum of the donor molecule and assigned to symmetric and asymmetric CCS stretching, CS stretching and SCS deformation (Table I). It seems that this anomaly shows a phase transition at about T_p ≈ 140K, probably a structural one.

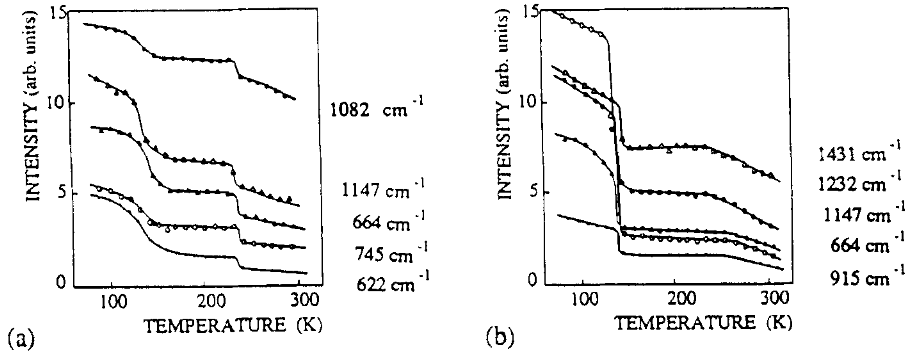


FIGURE 3 Temperature dependance intensities of selected bands: (a) $DClO_4$ and (b) $DCu(SCN)_2$

Our spectral investigation suggests that the 4,5-dihydro-1,3-dithiol-2-ylidene moiety changes its orientation at T_p. It should also be noted, that all observed changes are reversible and reproductible.

CONCLUSIONS

We have reported the temperature dependences of the IR absorption spectra of the salts derived from a giant analogue of TTF (D). Although the spectroscopy of powdered samples are not the best method for phase transitions investigations, we showed such phenomena in $DClO_4$ ($T_p \approx$ 220K) and $DCu(SCN)_2$ ($T_p \approx$140K). It seems that although there are dramatic changes in the intensities of most of the bands from high to low temperature, that for only selected bands can these intensity differences be attributed to the changes in the crystal structure or in the charge distribution.

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