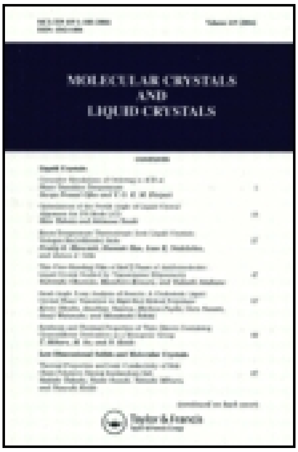

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Infrared and Resonance Raman Spectra of κ-$(BEDT\text{-}TTF)_2Cu(NCS)_2$ Organic Metals; H_8-, H_4D_4-, and D_8-(BEDT-TTF) Derivatives

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INFRARED AND RESONANCE RAMAN SPECTRA OF κ-(BEDT-TTF)$_2$ Cu(NCS)$_2$ ORGANIC METALS;H_8-,H_4D_4-, and D_8-(BEDT-TTF) DERIVATIVES

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Abstract We have carefully investigated the partially and completely deuterated bisethylenedithiolotetrathiafulvalene (BEDT-TTF) copper thiocyanate κ-phase salts (H_8-(BEDTTTF)$_2$ Cu(SCN)$_2$, H_4D_4-(BEDTTTF)$_2$Cu(SCN)$_2$ and D_8-(BEDTTTF)$_2$ Cu(SCN)$_2$ which exhibit a superconducting state around 10K as shown by a.c. magnetic susceptibility measurements. We have carried out IR absorption spectra on polycristalline samples at different temperatures and Resonant Raman scattering under visible excitations for investigating the Raman excitation profiles associated with the charge transfer bands. We have examined with a peculiar attention the electron-molecular vibration (e-mv) coupling involving the a_g vibronic modes. A final discussion concerns the role played by these intramolecular modes (Yamaji's model) for the onset of the superconducting state which exhibits a large and inverse isotopic effect in these materials.

INTRODUCTION

During these last years, several new series of molecular superconductors which are more or less two-dimensional (2d) electronic systems, have been discovered[1]. Among them, the so-called κ-phase compounds are the most interesting because they present both a quite original conducting phase and the highest superconducting transition temperatures ($T_c \leq 13K$) known in these materials. The prototype compound which has been the most widely investigated is the $(BEDT)_2$ $Cu(SCN)_2$ (BEDT is bis-ethylene dithiolotetrathiafulvalene) on which the isotope effect on T_c has been studied[2]. In the present work, we have examined the magnetic properties and the superconducting transition temperature of the partial or total substitution of hydrogen on the ethylene groups by deuterium. From a theoretical approach, YAMAJI[3] has postulated a BCS-type model for the occurence of a superconducting state based upon the attractive interactions between electrons which are mediated by the electron-molecular vibration (e-mv) coupling involving the vibronic (a_g type) modes. The coupling of these internal vibrations with different charge transfer excitations is the source of both IR and Raman activities[4,5] which are currently investigated. In this investigation, we have pursued the analysis of resonance Raman and infrared spectra of hydrogenated and partially or totally deuterated κ-$(BEDT\text{-}TTF)_2$ $Cu(NCS)_2$ crystals[6].

EXPERIMENTAL

The a.c. magnetic susceptibility has been determined between 5 and 15K for evidencing the SC phase transition on these compounds (Fig.1). Through the onset of Meissmer effect, we observe a rather large T_c increase with deuteration: $\Delta T/T_c \cong +5$ and 10% for $H_4D_4^-$ and D_8^- BEDT salts respectively. This comparison is valuable as long as the same experimental conditions are maintained because of the possible influence of growth conditions on T_c: in the present case, we observe a constant transition width which supports this point and confirms therefore this large inverse effect compared to the classical BCS prediction[1].

The IR spectra of H_4D_4 compound[6] observed for a polycristalline sample dispersed in KBr is shown on Fig. 2. As usual, we note an intense charge transfer band characteristic of a mixed valence state ('A' band, see inset of the figure 2) associated with several vibrational bands with a major signature around 1300 cm^{-1} which is attributed to a vibronic mode (a_g ν_4 C=C central and ring bonds)[6].

The preresonance and resonance spectra of powdered samples were recorded on a Dilor Z 24 triple monochromator using various emission lines of Spectra-Physics c.w. Kr^+ and Ar^+ lasers (676.4- 457.9 nm) in conjunction with the rotating disc technique.

The Raman excitation profiles (REPS) are extracted from intensity measurements on spectra of several homogeneous mixtures of powders in $RbClO_4$.

Considering the Raman excitation profiles, displayed on Fig. 3 for the ν(C=C) stretching modes in the D_8- derivative, we note three kinds of enhancement behaviors for the six observed Raman bands grouped in pairs. All the profiles have been normalized to the relative intensities when using λ_0 = 676.4 nm and similar enhancement factors were observed in the H_8- and H_4D_4- derivatives [6].

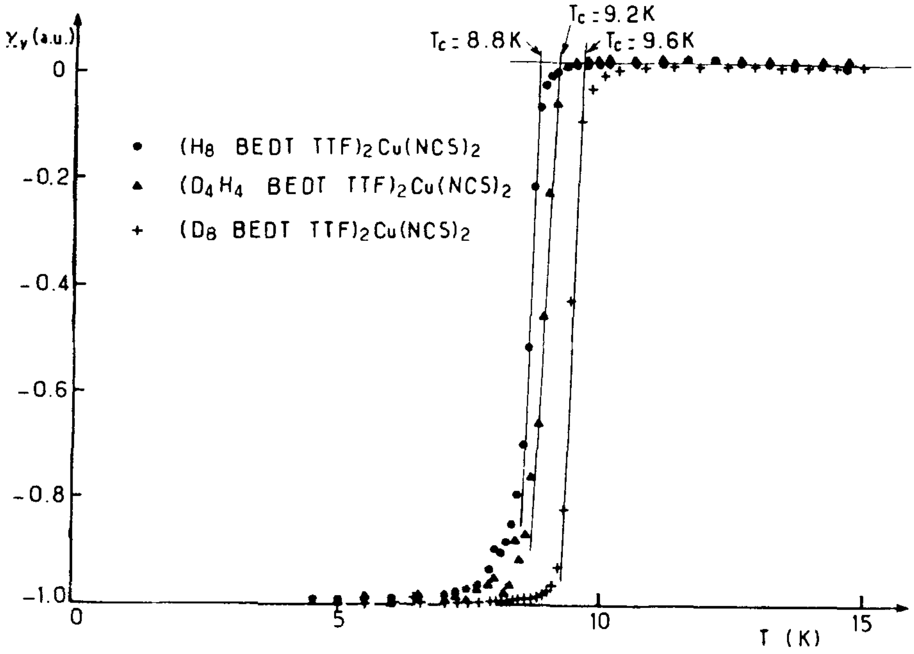

FIGURE 1 : Temperature dependences of the volume susceptibility χ_v (in arbitrary units) for the three investigated compounds. The onset of the SC state has been detected with a susceptometer under an a.c. field of 1 gauss oscillating at 666.7 Hz

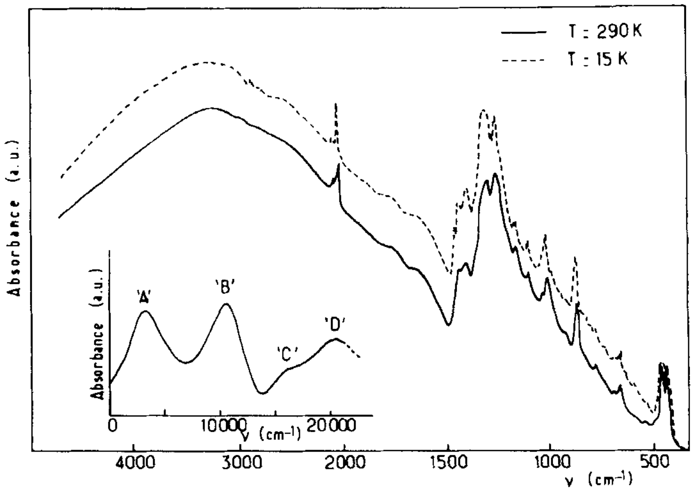

FIGURE 2 : κ-H_4D_4-(BEDT-TTF)$_2$Cu(NCS)$_2$: Temperature dependence of infrared absorption spectra of powder in KBr pellets (in inset, electronic absorption spectrum at room temperature).

DISCUSSION

These studies lead us to the attributions given in the Table I, where we have gathered the experimental IR and Raman frequencies for the considered stretching modes in relation with the degree of ionicity (ρ) defined from the oxidation state in the given salts, compared with the BEDT-TTF^0 and the BEDT-TTF$^+$ salt[7]. For the mixed valence systems, we have added to the considered salt, the results obtained by some other authors on one another superconducting salt, namely the β-(BEDT-TTF)$_2$ I_3[8]. In the Raman excitation profiles of bands at 1470-1450 and at 1420-1405 cm^{-1}, the resonances with the electronic transitions around 16100 cm^{-1} ('C' peak at 620 nm) and 19900 cm^{-1} ('D' peak at 500 nm) are observed (Fig.3). The excitation profiles of the bands 1506 and 1495 cm^{-1} are slightly different. For these bands, the resonance with the 'C' peak is also seen, but at higher excitation energies, a resonance mechanism with another electronic transition lying in the blue region above about 450 nm (i.e. 25000 cm^{-1}) is also found. The nature of this electronic transition is not clear at present. It might be related to the intramolecular BEDT-TTF$^+$ excitation observed at 22000 cm^{-1} in solution, shadowed by the broad conductivity band in the crystal spectra.

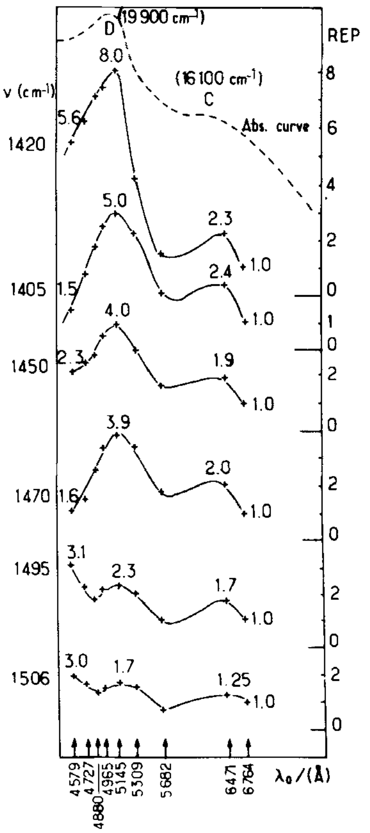

FIGURE 3 : Raman excitation profiles for the various components of the ν(C=C) stretching modes in κ-D_8-(BEDT-TTF)$_2$Cu(NCS)$_2$ at 300K. All the relative Raman intensities were normalized to unity at λ_0=676.4 nm ; arrows indicate the energies of laser excitations.

CONCLUSION

In spite of a large and inverse isotope effect observed on T_c, the partially deuterated salt behaves as both the completely hydrogenated and deuterated compounds in the normal state. The disorder introduced by the CH_2 and CD_2 groups and their progressive ordering at low temperature don't play apparently any crucial role.

We have shown the existence of strong e-mv couplings which influences both the Raman and IR lines which are the basis of the YAMAJI's model for superconductivity[9]. We don't find any peculiar feature associated with the partially deuterated molecule compared to the hydrogenated and deuterated molecules. In this series of compounds, we observe a regular increase of T_c[10] but this is not a general trend in the κ-phase compounds where the classical isotopic effect is also detected[1]. It turns out therefore that the YAMAJI's approach is not completely suitable for explaining the onset of superconductivity[3] but it rather appears that the mechanism of organic superconductivity should be mainly driven by electronic effects because the electron-electron correlations are significant in these materials[9].

IR				RAMAN				ASSIGNMENTS
ρ=0 (a)	ρ=0.5 (b)	(c)	ρ=1 (d)	ρ=0 (a)	ρ=0.5 (b)	(c)	ρ=1 (d)	(D2h)
1505	1445w	-----	1445w	-------	1420ms	1421	-------	ν_{27} (b_{1u})ring
	1408w	-----			1405w	------	-------	
			1344sh	1494	1470vS	1468		ν_3 (a_g) ring
					1450w	1439	1455	
	1320vs	1290					and	
-------			1398	1552	1506	-----	1431	ν_2 (a_g) central
					1495	1495		

TABLE I - Band wavenumbers (cm^{-1}) and assignments of the ν(C=C) stretching vibrations in κ-(BEDT-TTF)$_2$ Cu(NCS)$_2$ at 300K compared with BEDT-TTF and two of its salts.
a) according to KOZLOV et al.[8]
b) present work
c) Comparative assignments proposed from the Raman spectra at 22K and IR reflectivity IR spectra at 300K of β-(BEDT-TTF)$_2$ I_3[7].
d) (BEDT-TTF) Br salt[8]. According to KOZLOV's normal coordinate calculation, the ν_2 and ν_3 (a_g) modes are strongly coupled in this radical cation.

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