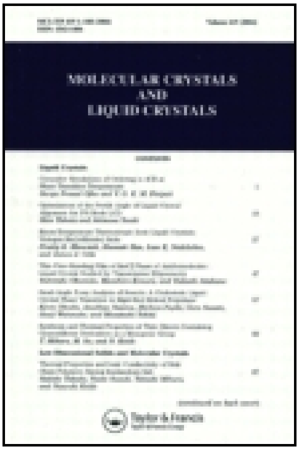

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ANOMALOUS VIBRONIC EFFECTS IN THE INFRARED SPECTRA OF THE ORGANIC CONDUCTOR Cu(DM-DCNQI)$_2$ AND ITS DEUTERATED ANALOG

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Abstract We report the observation of Fano-like antiresonance lineshapes for *ungerade* modes in the low temperature spectra of Cu(DM-DCNQI)$_2$ and its deuterated analog. Consideration of the existing structural and optical data leads us to conclude that the unusual vibronic coupling mechanism responsible for the observed lineshapes occurs via the effect of the vibrations on the $p\pi$–d hybridization of the conduction bands. This brings further support to the existence of a mixed-valence $Cu^{I/II}$ state in the studied compounds. The observation of additional vibronic effects attributed to electron charge oscillations induced by the a_g modes in Cu(DM-DCNQI-d_8)$_2$ suggests that the deuterium substitution favours the crossing of the border between the low temperature metallic and insulating phases.

INTRODUCTION

The Cu(2,5-R_1,R_2-DCNQI)$_2$ salts (DCNQI = N,N′-dicyanoquinonediimine) appear to be singular among the organic molecular conductors in that the stability of their metallic state down to very low temperatures seems to be related to the hybridization of their $p\pi$ bands, originating from the organic donors, with the atomic (or very narrow band) d levels of the Cu atoms.[1,2] The increase of dimensionality of the electronic interactions, required to overcome the Peierls instability of 1D metallic systems, is thus effected through the coordinated metallic counterions rather than by direct interstack interactions of the organic moieties as in the case of the well known BEDT-TTF salts.[3]

The issue of the presence of a mixed-valence state of the Cu atoms is still not completely settled[4-6] although some strong support comes from the observation of superlattice reflections at the wavevector $(0,0,c^*/3)$ in the insulating phase of Cu(MBr-DMDCNQI)$_2$,[5] i.e. the compound with R_1 = $-CH_3$ and R_2 = $-Br$. The fact that also the Cu(DM-DCNQI)$_2$ ($R_1 = R_2 = -CH_3$) and Cu(DMeO-DCNQI)$_2$ ($R_1 = R_2 = -OCH_3$) salts exhibit metal-to-insulator (M-I) transitions under moderate pressure[7,8] suggests similar electronic properties for these materials. Further support for the presence of mixed valence Cu ions in Cu(DM-DCNQI)$_2$ is provided by a recent refined analysis of XPS data.[6]

An important peculiarity of the structural changes accompanying the M-I transitions is that, beside the threefold increase of the unit cells along the stacking

c axis, the geometry of the distorted tetrahedral coordination of four DCNQI nitrogen atoms around the Cu ions also undergoes important changes.[1] This suggests that the coordination properties play a critical role in determining the electronic properties, most likely through their effect on the $p\pi$–d hybridization.

In this paper we address the above questions by investigating the IR spectra of Cu(DM–DCNQI)$_2$ and of its fully deuterated analog and their temperature evolution. Analyses of the powder IR spectra has been proved to be valuable for the probing of electronic and structural properties such as the opening of gaps at the Fermi level and the formation of charge density waves (CDW) and periodic lattice distortions in organic molecular conductors.[9] These possibilities arise from the appearance in the IR spectra of features attributed to the electron–molecular vibration (EMV) interactions and from the analysis of their band intensities and shapes. The results reported here demonstrate that the spectral features observed for the copper salts of DM–DCNQI are anomalous and appear to be related to the interactions between organic molecules and mixed–valence Cu ions.

TABLE I. Infrared powder[a] spectra of Cu(DMDCNQI)$_2$ and Cu(DMDCNQI-d_8)$_2$ at 300 K and at 10 K.

Cu(DMDCNQI)$_2^b$			Cu(DMDCNQI-d_8)$_2^b$	
($\tilde{\nu}$ / cm^{-1})^c		Assignment^d	($\tilde{\nu}$ / cm^{-1})^c	
2140, *m*	RT / LTF	$b_u\nu_{45}$	2140, *w*	RT / LTF
		$a_g\nu_3$	2130, *m*	/ LTV
		$a_g\nu_5$	1584, *w*	/ LTV
1542, *m*	/ LT			
1485, *vs*	RT / LTF	$b_u\nu_{47}$	1474, *vs*	RT / LTF
		$a_g\nu_7+$	1310, *br*	/ LTV
		$a_g\nu_8$	1280, *br*	/ LTV
1282, *w*	RT / LTF	$b_u\nu_{51}$		
		$b_u\nu_{49}$?	1227, *w*	RT / LTF
1184, *vw*	RT / LTF	$b_u\nu_{52}$		
		$b_u\nu_{50}$	1146, *w*	RT / LTF
1110, *w*	RT / LTF			
		$b_u\nu_{51}$	1054, *vw*	RT / LTF
		$b_u\nu_{53}$?	970, *m*	RT / LT
887, *vw*	RT / LTF	a_u?		
		$b_u\nu_{54}$?	818, 802, *w*	RT / LT
		$a_g\nu_{15}$	618, *m*	/ LTV
		$a_g\nu_{17}$	450, *w*	/ LTV
		$a_g\nu_{18}$	376, *m*	/ LTV

[a] Nujol and perfluorocarbon mulls on CsI window.

[b] RT = 300 K; LT = 10 K; F = Fano–like band shape. V = absorption of vibronic origin, intensity onset at about 80 K.

[c] Relative intensity: *vw* = very weak; *w* = weak; *m* = medium; *vs* = very strong; *br* = broad.

[d] G. Lunardi and C. Pecile, J. Chem. Phys., 95, 6911 (1991).

RESULTS AND DISCUSSION

The infrared spectra of Cu(DM–DCNQI)$_2$ powders suspended in mineral oil (Nujol or perfluorocarbon) exhibit only very weak vibrational structures on top of a broad absorption background originated by intra– and inter–band absorptions typical of highly conducting organic molecular materials. For the present case, single crystal polarized reflectance spectra, previously reported,[10] exhibit Drude edges both with incident electric vector parallel and perpendicular to the stacking **c** axis and have been analysed by Drude–Lorentz models to account for additional electronic transitions near the plasma frequencies.

Table I lists the frequencies of the vibrational bands observed in the powder spectra of the protonated Cu(DM–DCNQI)$_2$ and of the fully deuterated Cu(DM–DCNQI–d$_8$)$_2$ salt. At room temperature, only bands attributed to normally infrared active *ungerade* (mainly b_u) modes are observed. At low temperature the two compounds display different behaviors. The protonated one does not show additional bands. However the vibrational band shapes turn from regular absorptions to dispersive ones reminescent of Fano lineshapes.[11] A detailed view of the spectra recorded at various temperatures in the 1450–1570 cm^{-1} range is shown in Fig. 1. The deuterated Cu(DM–DCNQI–d$_8$)$_2$ exhibits a similar phenomenon on lowering the temperature but, in addition, it also shows the appearance of new bands. By comparison with similar bands observed for the low temperature semiconducting phase of Ag(DM–DCNQI)$_2$,[12] these new bands can be assigned

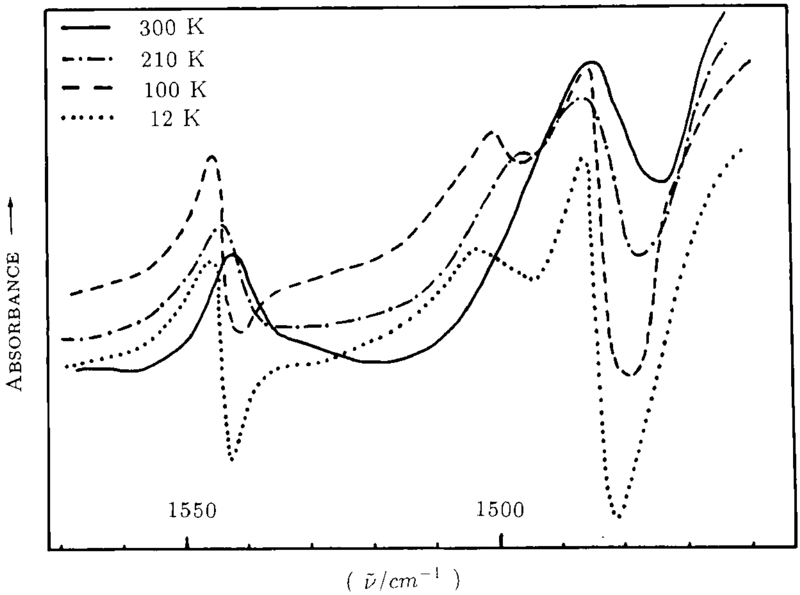

FIGURE 1 Infrared absorption spectra of Cu(DM–DCNQI)$_2$ powders at different temperatures in the 1450–1570 cm^{-1} spectral range.

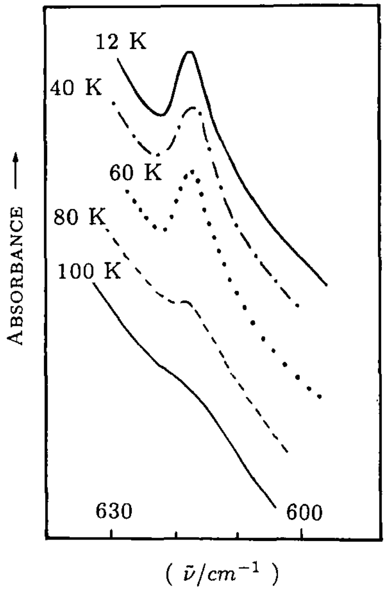

FIGURE 2 Temperature dependence of the powder absorption spectrum of $Cu(DM\text{-}DCNQI\text{-}d_8)_2$ in the 590–640 cm^{-1} spectral region.

to vibronic absorptions originated by the EMV coupling with totally symmetric a_g modes of DM–DCNQI–d_8. Fig. 2 shows one such band observed in the 590–640 cm^{-1} spectral range. In Table I the bands already present at room temperature (RT) that at low temperature (LT) exhibit a Fano lineshape are designated by LTF. Those appearing at low temperature in the deuterated compound and attributed to vibronic effects of the EMV coupling are denoted by LTV.

It is worth noting that investigation of the temperature dependence of the powder infrared absorption spectra of $Cu(DMeO\text{-}DCNQI)_2$, reported in detail elsewhere,[13] showed a temperature dependence of the *ungerade* modes similar to that observed for $Cu(DM\text{-}DCNQI)_2$ but no additional band at low temperature. The only important difference is that the Fano lineshape at low temperature is displayed only by bands located in a frequency range lower than in the DM–DCNQI salt.

A key consideration for the ensuing discussion is that, by itself, the observation of a Fano–type lineshape indicates a coupling between the vibrational mode displaying such a lineshape and an underlying electronic transition that overlaps the same frequency region. This can be shown in fairly general terms for vibrational modes giving rise to Hertzberg–Teller (non–Condon) coupling between the ground state and a very low energy excited state.[9] It is a consequence of the fact that the probabilities for the electronic and vibrational transitions add coherently and therefore give rise to mutual interference. The particular sequence of a peak and a dip, which characterizes the Fano lineshape, depends on the relative frequency location of the vibrational and electronic transitions. When the latter is higher in frequency than the vibrational mode, the dip occurs at a frequency higher than that of the peak. The opposite sequence is expected when the electronic transition frequency is lower than the vibrational one. Thus, the dispersive lineshapes observed for most *ungerade* modes in the low temperature spectra of protonated and deuterated Cu(DM–DCNQI)$_2$ imply a coupling of these modes with some very low energy electronic transition and we shall now discuss the possible nature of this transition and of the coupling mechanism.

The possibility that the *ungerade* modes of DM–DCNQI induce vibronic features in the spectra of Cu(DM–DCNQI)$_2$ via the so called *electron charge oscillation* mechanism[14] is ruled out both by the molecular symmetry and by the crystal structural properties. We recall that this mechanism requires that (i) the vibrational modes are able to modulate the conduction electron molecular orbital energy (the LUMO of the acceptor molecules) and (ii) the molecules in the crystal do not sit on inversion symmetry points so that a vectorial displacement of the electron charge can be induced by the coupled vibrational modes. None of the two conditions above is satisfied since the energy of a non degenerate LUMO can only be modulated by totally symmetric (a_g) vibrational modes and, in the structure of the copper salts, the DM–DCNQI units lie on inversion symmetry.[1]

As a consequence, one is forced to consider the alternative possible mechanism of electron–vibration coupling in molecular conducting materials, that is the modulation of the transfer integrals by the vibrational motions. Consideration of the crystal structural properties and of the symmetry classification of the optically active cell modes may help identifying a specific microscopic mechanism. We first note that the most remarkably dispersive lineshapes are observed for the b_u modes which consist of molecular deformations polarized in the molecular plane. As such, they are ineffective in modulating the integrals for the direct electron transfer between translationally equivalent DM–DCNQI units along the stacking **c** axis and, in any case, this would not lead to vibronic infrared activity. On the other hand the electron transfer interaction between acceptor molecules belonging to different stacks is very small, as indicated by the results of electronic band calculations[1] and by the highly 1D behavior of the isostructural silver salt.[10] The copper salts are however unique just because of the coordination properties of the metallic ions and the consequent $p\pi$–d hybridization. It is therefore natural to consider the possible role of the DM–DCNQI *ungerade* modes in modulating the transfer integral responsible for such band hybridization.

As already noted, the structural changes occurring at the M–I transitions of Cu(MBr–DMDCNQI)$_2$ [1,5] and Cu(DM–DCNQI)$_2$ [15] demonstrate the coupling between the electronic structure, notably the $p\pi$–d hybridization, and the geometry of the distorted tetrahedral coordination around the Cu ions. This means that any vibrational mode which induces changes in the coordination geometry is effectively coupled with the electron system. It appears that the b_u modes and, to a lesser extent, the a_u modes (polarized out of the molecular plane) do possess this ability. The symmetry analysis of the cell modes in fact shows that each *ungerade* molecular vibration gives rise to four crystal component of A_u, B_u and E_u symmetry. The A_u and the doubly degenerate E_u components are infrared active along the **c** axis and in the (**ab**) plane, respectively.

The single crystal infrared spectra polarized along the a axis reported by Yakushi *et al.*[10] show a very low frequency electronic absorption which has been attributed to intra–band transitions in the $p\pi$–d hybrid band. The oscillator strength of this band appears to increase markedly on lowering the temperature. The fact that the Fermi level lies in a hybrid band corresponds to the notion that the Cu ions are in a mixed–valence ($\mathrm{Cu}^{I/II}$) state and the average ionicity of the acceptor molecules is greater than 0.5. The threefold lattice distortion of the insulating phases[5] shows that Cu^{+}:Cu^{2+} = 2:1 and that the average charge of the DM–DCNQI molecules is $\rho = 2/3$. On account of this, a real space picture of the anomalous vibronic effect reported here could be as follows. The intra-band transitions observed in the a–polarized infrared spectra can be considered as a metallic–like intervalence transition in a Robin–Day class III mixed–valence compound.[16] The DM–DCNQI molecules act as the bridging ligands and provide the super–exchange pathway for the interaction between Cu ions sitting on symmetry equivalent environments. The molecular vibrations of b_u symmetry cause opposite deformations on two sides of the DM–DCNQI molecules. When b_u vibrations of different molecules in the unit cell combine to form infrared active A_u or E_u crystal modes, the coordination geometries around the four copper ions in the cell deform instantaneously in such a way as to induce an oscillating flow of charge among mixed–valence ions with an associated net dipole moment. Such a mechanism would account for the vibronic activity of the b_u modes and, by similar arguments, also of the a_u modes. The fact that the Fano–like bandshapes show up only in the low temperature infrared spectra (Fig. 1) is likely related with the corresponding increase of the oscillator strength of the intra–band transitions observed in the a–polarized single crystal spectra.[10]

In addition to the Fano lineshapes for *ungerade* modes, the low temperature IR spectrum of $\mathrm{Cu(DM\text{–}DCNQI\text{–}d_8)_2}$ shows vibronic absorptions attributable to electron charge oscillations driven by the EMV coupling with a_g modes (Fig. 2). In quasi–1D organic molecular conductors the appearance of similar bands on lowering the temperature signals the occurrence of Peierls–type M–I phase transitions.[9] In the particular case of $\mathrm{Ag(DM\text{–}DCNQI)_2}$, we have investigated the temperature evolution of these EMV induced bands and associated them to a dimeric and a tetrameric distortion of the DM–DCNQI stacks.[12] Such an interpretation is consistent with the formation of $4k_F$ and $2k_F$ CDW, respectively, in a quarter–filled band system. The coexistence of Fano type lineshapes in the deuterated copper salt implies a mixed–valence state for the Cu ions and a deviation of the band occupancy from 1/4, most likely towards 1/3 consistent with the interpretation given above for the $\mathrm{Cu(DM\text{–}DCNQI)_2}$ salt. The formation of either $4k_F$ or $2k_F$ CDW in this case would lead to a trimeric distortion of the stacks and the EMV induced absorption for this case are predicted to consist of a single component as opposed to two components for the case of a tetrameric distortion. Such prediction seems to be verified by the data in Fig. 2 whereas the spectra previously reported for $\mathrm{Ag(DM\text{–}DCNQI)_2}$ indeed showed a doublet structure of the vibronic absorptions.[12] We are therefore led to the conclusion that $\mathrm{Cu(DM\text{–}DCNQI\text{–}d_8)_2}$ undergoes an M–I phase transition at low temperature in agreement with recent results of resistivity measurements.[17]

The spectroscopic data reported here and their discussion provide experimental evidence of the coupling of the electronic states to changes in the coordination geometry around the copper ions and give further support to the existence of a mixed–valence state in the Cu(2,5–R_1,R_2–DCNQI)$_2$ salts. Comparison between protonated and fully deuterated DM–DCNQI salts suggests that the deuterium substitution may play the same role as the application of the very weak pressure required for Cu(DM–DCNQI)$_2$ to cross the border between the low temperature metallic and insulating phases. The fact that the spectra of Cu(DMeO–DCNQI)$_2$ display only the Fano lineshapes of *ungerade* modes but no sign of EMV induced absorptions is consistent with the greater stability of the metallic phase in this salt.

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