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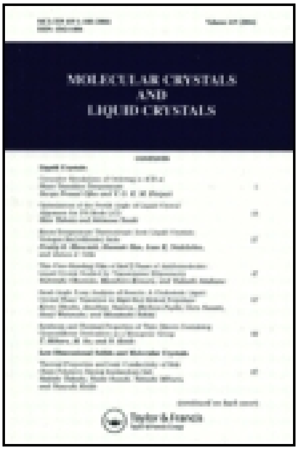

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Raman and infrared studies of the sharp 890 CM -1 mode in organic superconductors

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RAMAN AND INFRARED STUDIES OF THE SHARP 890 CM^{-1} MODE IN ORGANIC SUPERCONDUCTORS

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Raman and infrared spectra of several organic superconductors are presented, showing some unusual behaviours of a sharp line at 890 cm^{-1} in both spectra. These include a frequency shift below T_c, a positive deuterium isotope shift, frequency softening at low temperatures and sensitivity to lattice superstructure. It is proposed that either the ion or the neutral molecule has a distortion with a strong $\nu_{60}(B_{3g})$ mode component.

Keywords: Raman; infrared; organic; superconductors; electron-phonon

INTRODUCTION

Figure 1 shows the Raman spectra of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br taken with a visible laser and with an infrared laser [1]. Eleven of the twelve totally-symmetric (A_g) modes of vibration, assuming D_{2h} symmetry, are indicated on the visible spectrum. The infrared-laser spectrum is a resonant spectrum and not all of the A_g modes are seen. The resonant modes which are seen are also the modes which are very intense in the infrared spectrum, where they have been activated through an electron-phonon interaction. This may be seen in Figure 2. The most intense of these A_g modes are $\nu_3(A_g)$, and $\nu_9(A_g)$. They have been shifted down in frequency in the infrared spectrum again due to the electron-phonon interaction.

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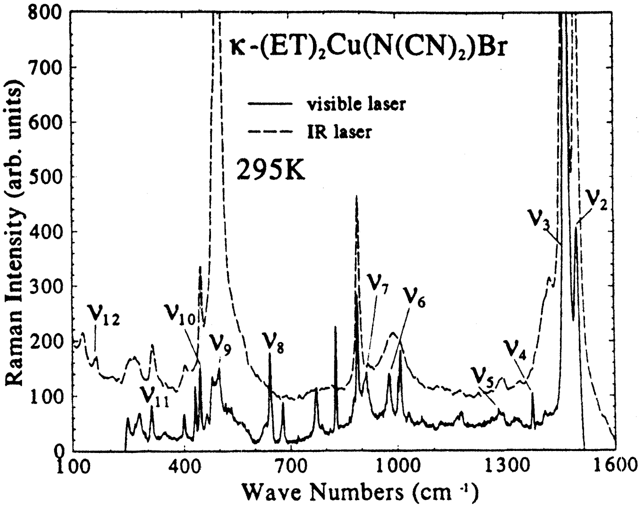

FIGURE 1 The Raman spectra taken with two lasers.

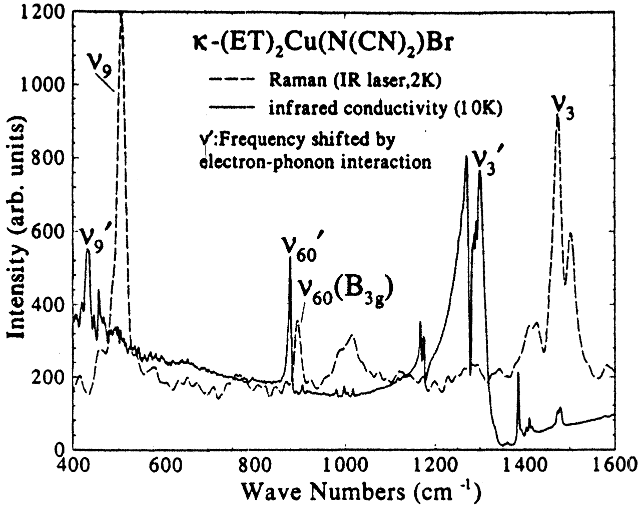

FIGURE 2 The Raman and infrared spectra (from [1]).

The electronic transition responsible for the resonant Raman spectrum is clearly the same as that producing the infrared activity. For the totally-symmetric modes the transition is the transfer of charge between two molecules in a dimer, oscillating out of phase. The totally-symmetric modes

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change the size of the molecule, as does the amount of charge on the molecule. Charge therefore moves from the molecule decreasing in size to the molecule increasing in size. The infrared dipole is perpendicular to the molecular plane, as may be seen in the α and β-phase materials, where the molecules are arranged in stacks.

The sharp line near 890 cm^{-1} in Figures 1 and 2, on the other hand, appears not to be due to an A_g mode. We have assigned it to $\nu_{60}(B_{3g})$. This paper presents some new and some previously-published unusual properties of this spectral line and we attempt to explain them. (In our earlier papers we assigned it to $\nu_{49}(B_{2u})$.)

ASSIGNMENT

The assignment has been based on several infrared and Raman studies of various compounds, involving five different isotopic substitutions [2–4]. The measured shifts in two conducting salts along with the calculated shifts of some modes in the neutral ET compounds are listed in Table 1. For a summary of the reasoning behind the $\nu_{60}(B_{3g})$ assignment see [4]. The atomic displacements in the $\nu_{60}(B_{3g})$ normal mode are drawn below in Figure 3.

TABLE 1 Experimental Frequencies and Shifts of the "890 cm^{-1}" Feature in Two Conducting ET Salts, κ-$(ET)_2[Cu(NCS)_2]$ and κ-$(ET)_2Cu[N(CN)_2]Br$, Together with the Calculated Frequencies and Shifts of Modes Which have Approximately the Same Frequency in Neutral ET.

	Natural ν	$^{13}C(2)$ $\Delta\nu$	$^{13}C(4)$ $\Delta\nu$	$^{13}C(6)$ $\Delta\nu$	$^{34}S(8)$ $\Delta\nu$	$^{2}H(8)$ $\Delta\nu$
Experimental						
Infrared	881	2	2	25	4	+7
Raman	890	+1	3	26		+9
ET Calculated						
$\nu_6(A_g)$	983	1	1	32	6	6
$\nu_7(A_g)$	918	0	21	1	1	188
$\nu_{48}(B_{2u})$	904	7	0	25	7	2
$\nu_{49}(B_{2u})$	872	20	0	27	5	2
$\nu_{60}(B_{3g})$	885	2	0	26	6	4

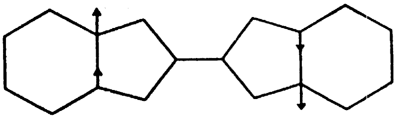

FIGURE 3 Atomic displacement vectors for $\nu_{60}(B_{3g})$ normal mode of vibration, assuming D_{2h} point-group symmetry.

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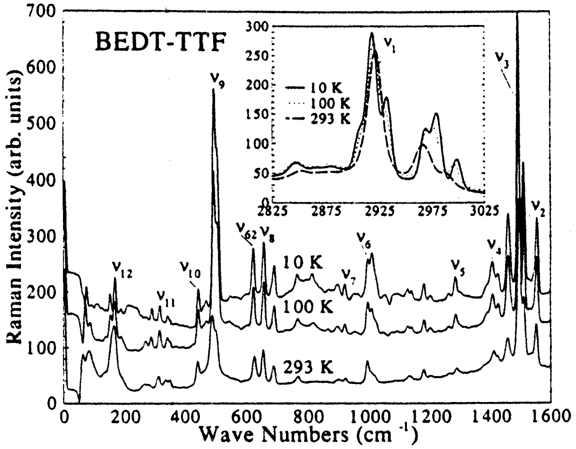

FIGURE 4 The Raman spectra of neutral ET at three temperatures, taken with an infrared laser [5].

Another consideration in the assignment of $\nu_{60}(B_{3g})$ is the fact that all 12 of the totally-symmetric A_g modes are observed in the spectrum of the neutral ET compound, along with their expected isotope shifts. The sharp 890 cm^{-1} line is not present in this spectrum but appears only in the spectra of the ET salts. (See Figure 4).

EFFECT OF T_C

Figure 5 shows the frequency of the $\nu_{60}(B_{3g})$ feature in the Raman spectrum of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br as a function of temperature [1]. A frequency increase of 2.2 ± 0.4 cm^{-1} is observed at temperatures below the T_c of 11.6 K. This increase was measured in two different refrigerators, a Janis and a Heli-Tran. In the former the sample was immersed in superfluid liquid helium at the lowest temperature. When the sample is rapidly cooled, which suppresses the superconductivity, the frequency shift is no longer present, (see Figure 5). Clearly the shift is superconductivity-induced. We see no shift in any of the other strong features in our spectrum, although shifts have been measured by Pedron et al. [6] in the low-energy lattice modes.

In a similar experiment with κ-(BEDT-TTF)$_2$[Cu(NCS)$_2$] we observed no frequency shift but it is possible that we were not able to cool it sufficiently slowly. We did, however, observe a shift in α_t-(BEDT-TTF)$_2$I$_3$ below the T_c of 8 K. This time the shift was a ***decrease*** of 1.7 ± 0.4 cm^{-1} in the upper component of the doublet structure (see Figure 6 below).

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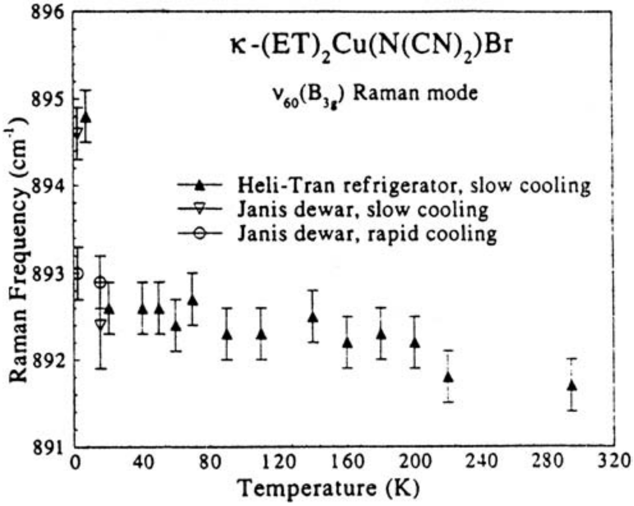

FIGURE 5 The frequency of the ν_{60}(B$_{3g}$) Raman feature as a function of temperature.

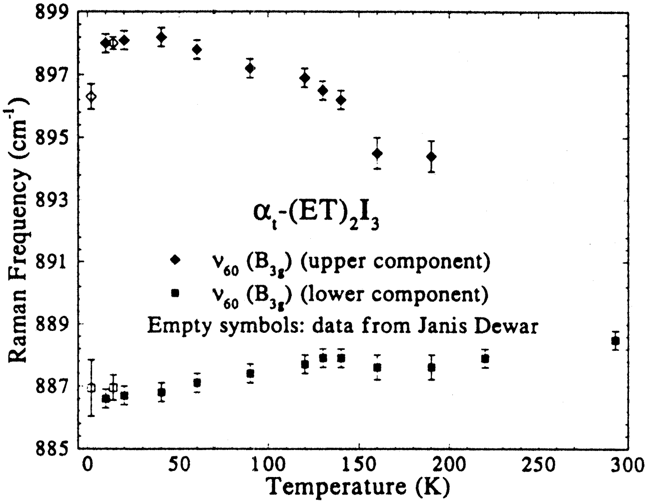

FIGURE 6 The frequency of the two components of the ν_{60}(B$_{3g}$) feature in α_t-(BEDT-TTF)$_2$I$_3$ as a function of temperature.

DEUTERIUM ISOTOPE SHIFT

In all of the ET compounds investigated so far we measure a frequency *increase* of 7–19 cm^{-1} of the $\nu_{60}(B_{3g})$ feature upon deuteration. The same increase is measured in the Raman and in the infrared spectra. This shift may be seen for κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br in Figure 7 below.

The hydrogen atoms are not directly involved in the $\nu_{60}(B_{3g})$ ring deformation of Figure 3. The above shift must result from a lattice effect involving the interaction of the ethylene groups with those of their nearest ET neighbours as well as the adjacent anions.

SUPERSTRUCTURE

Figure 7 above shows the $\nu_{60}(B_{3g})$ doublet seen in β-(BEDT-TTF)$_2$I$_3$. This doublet develops below 190 K, at which temperature neutron [7] and x-ray studies [8] have shown an incommensurate structural modulation of the triiodide anions and ET molecules. However, no splitting is observed for any other of the strong Raman lines, indicating that $\nu_{60}(B_{3g})$ is particularly sensitive to effects from the surrounding lattice.

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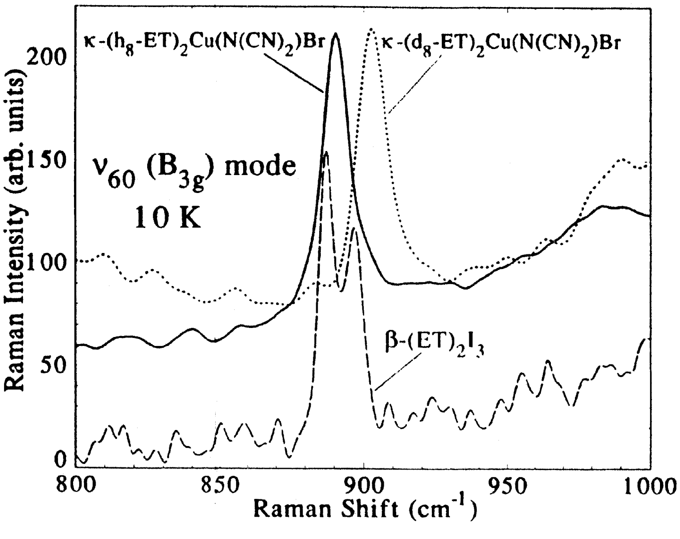

FIGURE 7 The Raman line due to $\nu_{60}(B_{3g})$ in protonated and deuterated κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br, as well as in β-(BEDT-TTF)$_2$I$_3$, all at 10 K.

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TEMPERATURE EFFECT

Figure 8 below shows the effect of temperature on the frequencies of the Raman lines due to the $\nu_{60}(B_{3g})$ and $\nu_9(A_g)$ modes in κ-(BEDT-TTF)$_2$[Cu(NCS)$_2$]. Both of them show a definite softening below about 100 K at which temperatures evidence has been found for magnetic fluctuations. An interaction between the fluctuating antiferromagnetism and these phonon modes may therefore be responsible for these softenings. (In Figure 5 no softening is seen for $\nu_{60}(B_{3g})$ in κ-(BEDT-TTF)$_2$Cu [N(CN)$_2$]Br but the very flat temperature dependence of the frequency may be due to the competition between the magnetic softening and the usual lattice hardening.)

DISCUSSION

How therefore does $\nu_{60}(B_{3g})$ become infrared-active and strongly Raman resonant? Because of the nature of the mode we have previously speculated that it may involve transfer of charge not between dimers but between other neighbouring ET molecules. However, inspection of the infrared spectra from α and β-phase materials shows that the $\nu_{60}(B_{3g})$ infrared line is also polarized along the ET stacks. Kaplunov and

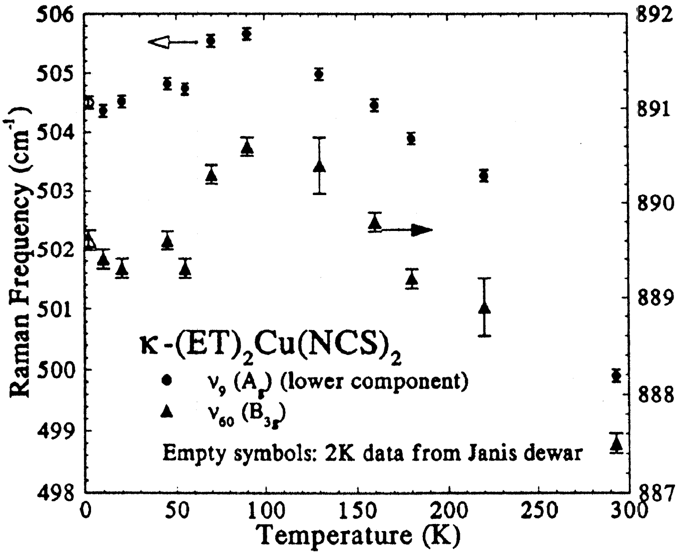

FIGURE 8 The frequencies of two Raman lines in κ-(BEDT-TTF)$_2$[Cu(NCS)$_2$] as a function of temperature.

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Lyubovskaya [9] have discussed electron-vibrational bands involving non-totally symmetric phonons. If the symmetry of the neutral ET molecule and the ET^+ ion are both totally-symmetric then only A_g phonons are allowed. If, however, one of them is not totally-symmetric then other phonons are allowed. This means therefore that in these salts either the ET molecule or the ET^+ ion has a small ring deformation with a strong $\nu_{60}(B_{3g})$ component. Since the neutral ET molecule is already distorted in a "boat-like" structure, then it may also have this ring deformation. Whichever of the two is distorted, the electron-phonon mechanism is the strong and obvious, as the charge will oscillate between the two in a dimer as they vibrate out of phase in the distortion mode, giving rise to infrared activity and Raman resonance.

The distortion would explain the different intensities of the Raman $\nu_{60}(B_{3g})$ line in the molecular and ionic spectra. The removal of free carriers, involved in the presence or absence of the distortion, in the superconducting phase may explain the frequency shift below T_c. If the distortion depends not only on charge but on the presence of nearest ET neighbours, which interact through the ethylene groups, then the positive deuterium shift may be understood. The distortion would of course be sensitive to any lattice superstructure, and perhaps the doublet in the triiodide results from separate ionic and neutral-molecule vibrations. Certainly with strong electron-phonon coupling the mode would be sensitive to the ordering of electron spins in antiferromagnetism as seen in several compounds and also in the $\nu_9(A_g)$ Raman line.

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