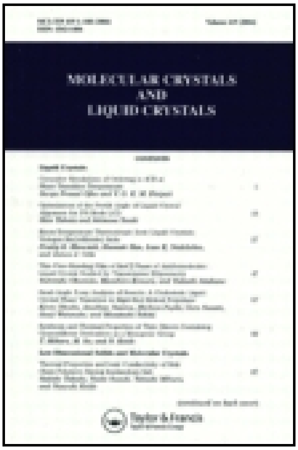

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Raman Study at Low Temperature of Polyiodidesin the Series DIPSφ_4

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RAMAN STUDY AT LOW TEMPERATURE OF POLYIODIDES IN THE SERIES DIPSΦ_4

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We report low temperature Raman scattering study of polyiodides in a series of DIPSΦ_4 (tetraphenyldithiapyranylidene). Iodine species consist of I_3^- or I_3^- and I_5^- ions and at low temperature, Raman spectra reveal new features. A splitting of the stretching vibration of the I_3^- ion is observed, which depends on the iodine concentration, in connection with the conductivity value. This phenomenon can be interpreted in terms of an interaction between two I_3^- ions located on the same iodine column.

INTRODUCTION

Organic quasi-one dimensional conductors can be divided into different classes, in particular charge transfer complexes and radical-ion salts. In the case of charge transfer complexes, both the donor and acceptor stacks participate in the electrical conductivity. The class of cation salts has been developped more recently, oxidyzing π -donors with halogens for example. In this case, only donor stacks participate in the conductivity.

The synthesis of polyiodides from DIPSΦ_4 (tetraphenyldithiapyranilidene) is performed by direct oxidation or by a disproportionation method[1].

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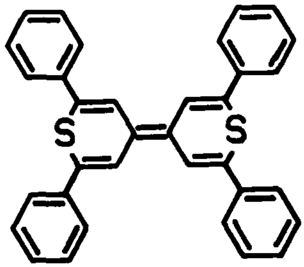

DIPSΦ4

Two conducting salts have been synthetized and characterized[1,2].

Salt 1: DIPSΦ$_4$, 2.28I σ = 250 (Ω cm)$^{-1}$

Salt 2: DIPSΦ$_4$, 3.3-3.45 I σ = 2 (Ω cm)$^{-1}$

Oxidation performed with an excess of iodine yields salt 3 which is an insulating material:

Salt 3: DIPSΦ$_4$, 6I σ = 10^{-6} (Ω cm)$^{-1}$

Two polyiodides have been described elsewhere by Isett et al.[3] under the name $\Phi_4DTP(I_3^-)_{0.75}$ and $\Phi_4DTP(I_3^-)_{1.06}$ where Φ_4DTP is similar to DIPSΦ$_4$.

CHARACTERIZATION

The two conducting salts (1 and 2) have been characterized using several different techniques such as: X-ray diffraction, X-ray diffuse scattering, optical absorption (visible and IR) and Raman scattering. Salt 3 was only obtained in powder form and therefore was not studied in details. It has been shown that salts 1 and 2 which are composed of green and violet needles respectively are not isomorphous. Salt 1 (DIPSΦ$_4$, 2.28I) has a tetragonal structure (a = 19.70 Å, c = 3.71 Å) while salt 2 (DIPSΦ$_4$, 3.3-3.45I) is orthorombic (a = 31.02 Å, b = 54.82 Å, c = 3.70 Å). Also, in connection with Raman experiments, iodine columns composed of I_3^- ions have been detected in salt 1 while in salt 2, iodine columns of two different nature have been seen. The anisotropy in electrical conductivity has been measured recently[4]. In salt 1, σ//b/σ⊥b (where b is the stacking axis) is found to be of the order of 10^3-10^4. Salt 2 is less anisotropic and $\sigma//b/\sigma\perp b$ is less than 10^3. Therefore, salt 1 (DIPSΦ_4, 2.28I) turns out to be an organic crystal presenting good quasi one-dimensional properties.

Raman spectroscopy at 77K revealed previously I_3^- ions (stretching vibration at 107 cm^{-1}) in salt 1 and both I_3^- and I_5^- ions in salt 2, in agreement with X-ray experiments.

RAMAN STUDY AT LOW TEMPERATURE

The new results reported here are those obtained using Raman scattering at liquid helium temperature. We have investigated the three following samples: salt 1 (DIPSΦ_4, 2.28 I), salt 2 (DIPSΦ_4, 3.3-3.45I) and salt 3 (DIPSΦ_4, 6I). Experimental conditions have been described previously[2], except the cryostat which was an immersion one using either liquid helium or helium gas as the exchange factor. Raman spectra have been recorded with an improved spectral resolution (1.7 cm^{-1} for λ_{exc} = 514.5 nm).

Salt 1 (DIPSΦ_4, 2.28I)

The Raman spectrum obtained is shown Figure 1.

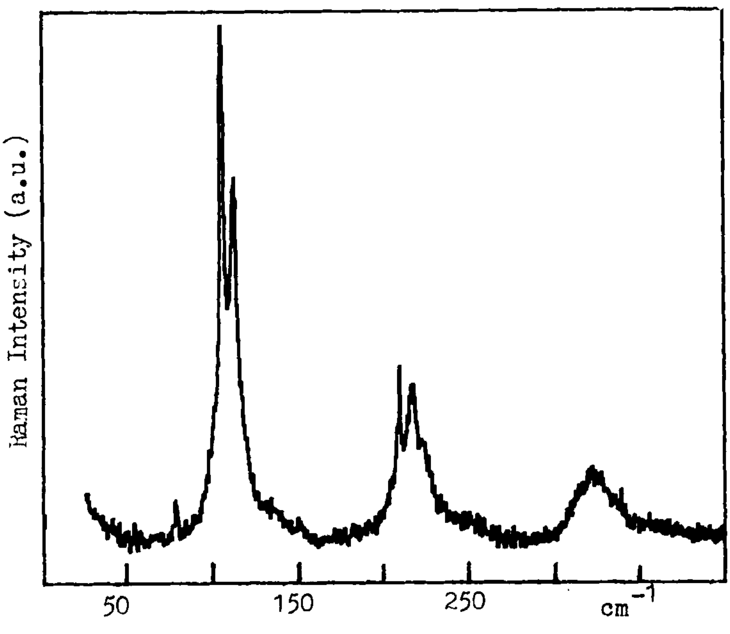

Figure 1 Raman spectrum at T = 4.2K of DIPSΦ_4, 2.28 I for $\lambda_{exc.}$ = 514.5 nm.

Two intense peaks are observed at 105 and 112 cm^{-1}. The previous Raman study at 77K revealed only one peak at 107 cm^{-1} assigned to the stretching vibration of the I^- ion[2]. Overtones and additive frequency lines are clearly[3] observable at 210, 217 and 224 cm^{-1} on one hand and 332 cm^{-1} on the other hand. No signal is observed in the spectral region between 140 and 170 cm^{-1}.

Salt 2 ($DIPS\Phi_4$, 3.3-3.45I)

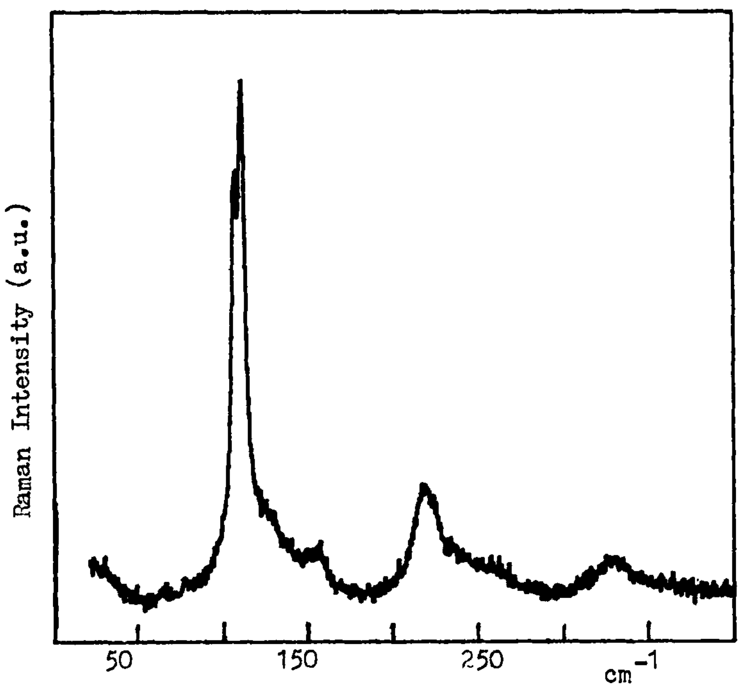

Figure 2. Raman spectrum at 4.2K of $DIPS\Phi_4$,3.3 3.45I for $\lambda_{exc.}$=514.5 nm

In this case, the two peaks are observed at 107 and 112 cm^{-1} respectively showing a splitting of 5 cm^{-1} while the first overtone is structureless. A weak band is also detected at 157 cm^{-1}, as previously reported and assigned to I_5^- ions[2].

Salt 3 ($DIPS\Phi_4$, 6I)

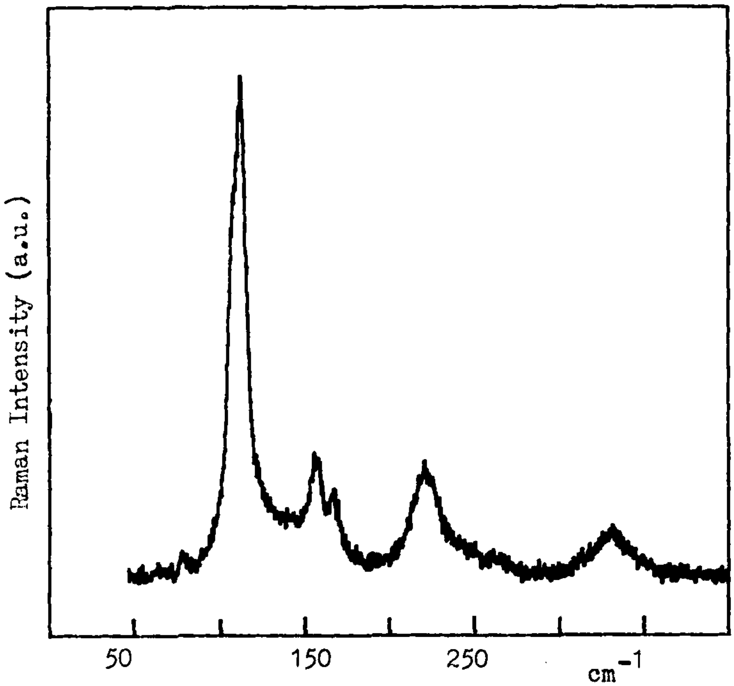

Figure 3. Raman spectrum at 4.2K of $DIPS\Phi_4$, 6I for $\lambda_{exc.}$ = 514.5 nm.

The main Raman line is peaked at 112 cm^{-1} but a shoulder is clearly present on the low frequency side at 108 cm^{-1}

(a better spectral resolution allows us to distinguish between these two peaks). Overtones are also observed at 224 and 335 cm^{-1}. In the region 140 - 170 cm^{-1}, two weaker peaks are detected at 157 and 167 cm^{-1}.

DISCUSSION

The most important result obtained in this study is the splitting, at low temperature, of the Raman line assigned to the totally symmetric stretching vibration of the I_3^- ion. The fact that we observe both the overtones and the additive combination frequency peak (210, 217 and 224 cm^{-1} for example for salt 1) excludes any possibility that two slightly different I_3^- ions are present in the sample. Such as splitting comes from a breakdown in symmetry with respect to the $D_{\infty h}$ symmetry for the I_3^- ion. This has already been observed in some other solid materials such as Et_4NI_3, Bu_4NI_3[5]. Many reasons can be argued to explain this phenomenon. In these particular cases where I_3^- ions are located in columns as shown by X-ray experiments, it is more likely that two I_3^- ions interact together. This interaction can lead to a statabilization of donor stacks. Moreover, it is worth noting that the stronger the interaction (7 cm^{-1} for $DIPS\Phi_4$, 2.28I) and the higher the conductivity (σ = 250 $(\Omega\ cm)^{-1}$ and $\sigma_{//}/\sigma_{\perp} \simeq 10^3$-$10^4$). For salt 2 ($DIPS\Phi_4$, 3.3 - 3.45I), a weaker interaction is observed and σ = 2$(\Omega\ cm)^{-1}$ and $\sigma_{//}/\sigma_{\perp} \simeq 10^3$. In the case of salt 3 ($DIPS\Phi_4$, 6I), an even weaker interaction leads to an insulating material ($\sigma = 10^{-6}$ $(\Omega\ cm)^{-1}$). It is somewhat speculative to use the above correlation in case of salt 3 which was not obtained in a crystalline form. Nevertheless, in this salt, the iodine species (I_3^- and I_5^-) can be arranged in the less ordered way by comparison to the two other cases. In fact, different I_5^- ions are detected in Raman scattering (bands at 157 and 167 cm^{-1}). Moreover, ESCA results[6] confirm the presence of I_5^- ions in high concentration in salt 3.

In conclusion, the interaction between two I_3^- ions observed by Raman scattering in polyiodides in the series of $DIPS\Phi_4$ seems to be correlated with the electrical conductivity. Similar studies on other polyiodides are under way.

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