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Observation of Davydov splitting in PTS polydiacetylene crystal spectra

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LETTERS TO THE EDITOR

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COMMUNICATIONS

Observation of Davydov splitting in PTS polydiacetylene crystal spectra[a)]

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The electronic spectra of polydiacetylene crystals have often been typified by poly-2, 4-hexadiyne-1, 6-diol-bis-(*p*-toluene sulfonate) (PTS). The spectra of crystals of this polydiacetylene have been unique in that they have displayed a pronounced "doubling" of the 300 K spectral bands at temperature below 170 K. The reflection bands are also observed to undergo a continuous red shift with continued decrease of temperature. The reflection band observed at lowest energy at 300 K is resolved at 77 K into two clearly separated bands at 15 700 cm^{-1} (Ib) and 16 050 cm^{-1} (IIb).[1–5] A recent study by modulated piezoreflection spectroscopy on PTS crystals demonstrated that this "doubling" persists to 300 K.[5] The phenomenon is best explained by recent x-ray crystallographic studies which show that at 170 K the unit cell of the PTS doubles along the *c* axis.[6] This gives two pair of polymer chains in the low temperature unit cell which are translationally inequivalent and which sit at different sites. One pair is face centered while the other is located at the cell edges. This creates two energetically different environments for the different pairs and thus a splitting of the spectrum such as that actually observed may be expected. The existence of the doubling at 300 K may be attributed to persistence of the 170 K phase.

In contrast to the spectrum for light polarized along the polymer chain which lies parallel to the *b* axis in the $P2_1/c$ unit cell,[7] that reported for the perpendicular direction in (001) showed a flat response.[1] In the Frenkel exciton model of the PTS crystal, a Davydov split component would be expected with a polarization in the *ac* plane.[8] The failure to detect a component polarized in the *ac* plane would not necessarily be deemed unusual since the large interchain separation of 7.5 Å could be expected to lead to a negligibly small crystal interaction. The lack of observation of such structure could be also completely rationalized by taking the transition moment to be polarized parallel to the *b* axis and excluding vibrationally induced changes in polarization. To assure that no *a*-axis structure exists, an effort to locate such structure was made. This Communication reports the observation of *a*-axis polarized structure in the electronic spectrum of PTS.

Polarized normal incidence specular reflection spectra have been obtained for light polarized parallel and perpendicular to the chain direction and are shown in Fig. 1. In the *a* axis 300 K spectrum a small broad peak is observed at 15 900 cm^{-1} at a relative reflectivity of 7.65 ± 0.05% which is only 0.5% above the background reflectivity. The *a*-axis piezoreflection[9] spectrum at 300 K is shown over the region of interest. A definite change of slope is observed at 15 950 cm^{-1}.

At 77 K the *a*-axis structure is observed to red shift and become resolved. The lowest energy band at 300 K splits into two prominent peaks at 15 650 (Ia) and 15 870 (IIa) cm^{-1} and a weak peak at 16 225 cm^{-1}.[10] The associated reflectivities are 7.1, 6.4, and 5.8% (all ± 0.1%). Additional weak structure is observed at 16 670, 16 850, 17 120, and 17 320 cm^{-1}. The frequencies of the two prominent peaks are separated by 220 ± 25 cm^{-1} which is on the order of the separation indicated by the 300 K piezoreflection spectrum.

Measurements were obtained at 50 cm^{-1} intervals. The same frequencies were used for the scan in each spectrum. Data were obtained by ensemble averaging until a 95% confidence level was achieved. Spectra were taken from two different sets of crystals,[11] each of which was photometrically aligned under crossed Glan–Thompson calcite prisms. The 300 K spectra were taken without windows between the sample and the reflectometer lens thereby establishing that the observed structure does not arise from external optical effects.

The pronounced peak occurring at 15 900 cm^{-1} in the *a*-axis polarization may be assigned as the Davydov component of the *b*-axis 300 K polarized band. The piezomodulation spectrum of the 300 K *a*-axis spectrum indicates structure at 15 850 and 15 970 cm^{-1}. The apparent separation of these bands is only 120 cm^{-1} at room temperature. The lowest energy structure at 15 830 cm^{-1} in the 300 K *b*-axis piezomodulation spec-

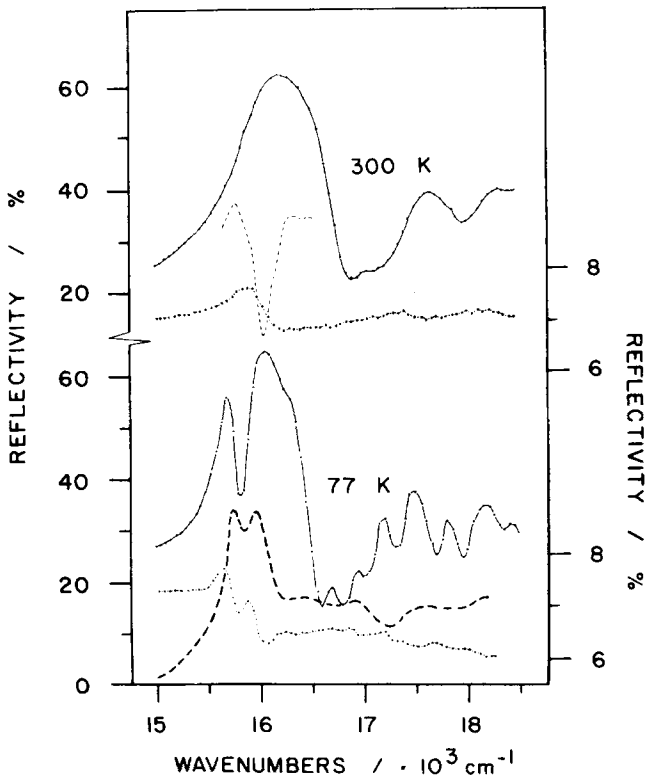

FIG. 1. Specular reflection spectra of PTS: 300 K spectra are displayed above the break in the ordinate; b-axis (upper curve, left ordinate), a-axis (lower curve, right ordinate), and a-axis piezoreflection (dashed line). 77 K spectra are shown below the break in the ordinate; b axis (upper curve, left ordinate) and a axis (lower curve, right ordinate). ϵ_2 curve from Kramers–Krönig transform of 77 K b-axis spectrum (heavy dashed line; arbitrary ordinate). Bandpass is 30 cm^{-1}.

trum suggests a splitting which is on the order of the resolution of the experiment.

The 77 K data are more instructive. From the known energy of Ib, the splitting for the lowest energy components is found to also be on the order of the resolution of the experiment. However, the apparent splitting between IIb and IIa is 180 ± 25 cm^{-1}. Comparison of the 77 and 300 K a-axis spectra indicates that there is also significant thermal dependence of the intensities and frequencies of the a-axis system.

While splittings are apparent from the reflection spectra, meaningful values can only be obtained through Kramers–Krönig transforms of the reflection spectra. The transform of the b-axis reflection spectra have been previously reported and are in agreement with our transforms of the b-axis spectra. The a-axis spectra have also been transformed for both the 300 and 77 K spectra. For the 300 K spectrum a peak is observed in ϵ_2 at 15 840 cm^{-1} (b-axis) and 15 940 cm^{-1} (a-axis) giving a Davydov splitting of 110 cm^{-1}. At 77 K peaks in the a-axis spectrum of nearly equal intensity appear at 15 740 cm^{-1} (Ia) and 15 940 cm^{-1} (IIa) whereas the peaks Ib and IIb appear with nearly equal intensities at 15 600 and 15 860 cm^{-1} in the b-axis polarization. Thus the Ia–Ib splitting is 140 ± 25 cm^{-1} and that for IIa–IIb is 80 ± 25 cm^{-1}.

The dichroic ratios for both sets of peaks are $a/b \sim 0.02$. This indicates a polarization of the transition of about 9° off the b axis which is similar to that found for the TCDU polydiacetylene crystal.[12] It is also consistent with an excitonic model of the polymer.[12,13]

These data show that Davydov splittings do exist in the PTS crystal spectra in spite of the large interchain separation. While a satisfactory microscopic model for PTS does not yet exist, location of the Davydov components will necessarily affect current interpretations.

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