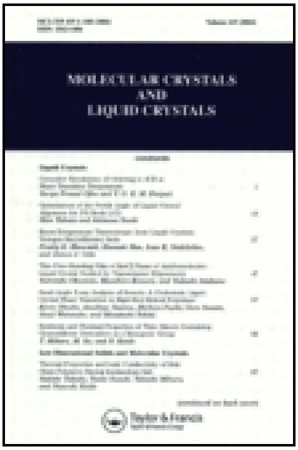

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Polymorphism of Crystalline Thiophene: Infrared and Raman Spectra

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Polymorphism of Crystalline Thiophene

Infrared and Raman Spectra

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The four solid modifications of thiophene have been investigated by infrared and Raman spectra. Infrared spectra in polarized light on oriented polycrystalline samples of the forms III and IV cooled at 77 K have also been measured. A new evidence of the forms II and III is presented.

From the spectroscopic data it has been possible to establish that all the crystalline forms belong to the orthorhombic system and that the transition mechanism probably involves a slight rearrangement of the molecules in the unit cell.

INTRODUCTION

Polymorphism of crystalline thiophene[1] has been the object of considerable interest of spectroscopists,[2–5] the main purpose of their studies being the determination of the spectroscopic and structural features of the four crystalline forms. In fact, apart from an X-ray diffraction study by Abrahams and Lipscomb[6] on the first phase and an old paper by Bruni and Natta,[7] no other crystallographic work is reported in the literature.

The analysis of the vibrational spectra could be in principle very useful to get information about the crystal structure of those forms which have never been investigated by X-ray diffraction. However, the structural conclusions reached by different authors by means of infrared spectroscopy are not in agreement with each other and this fact is to be related, at least in part, to the kinetics of the phase transitions in solid thiophene. We have discussed this problem in a recent paper[8] and we have suggested a reproducible method for isolating all the forms. On the basis of these experimental findings we have measured the infrared and Raman spectra of all the four phases as well as the infrared spectra in polarized light of the forms III and IV.

In this paper we report on the analysis of these vibrational data and we present some conclusions on the crystal structures of the phases and on the transition mechanism among them.

EXPERIMENTAL

Thiophene from Carlo Erba was repeatedly distilled and its purity was checked by gas-chromatography. Raman spectra were registered with a Cary 81 spectrograph equipped with an Argon ion Laser source selecting the 4880 Å line as exciting light. The low temperature cell used was designed for observation of the scattered light at 90°.[9] Polycrystalline samples for infrared spectra were prepared by vapor deposition on a cold window at 77 K. The infrared spectra in polarized light were measured on oriented samples grown by crystallization of liquid films between two CsI windows. The temperature of the samples was monitored by a copper-constantan thermocouple held in contact with the windows by an indium gasket. Infrared spectra were registered with a Perkin–Elmer model 225 grating spectrophotometer with an average spectral slit-width of 1 cm^{-1} and using a conventional low temperature cell.

RESULTS

The vibrational assignment of gaseous thiophene has been discussed both on experimental[10] and theoretical[11,12] grounds and the main features seem well established. The assignment of the crystal reported in Table 1 has been made on this basis. No additional information was obtained from the spectra in polarized light since infrared bands of the same symmetry species do not show a coherent dichroism and the crystal structure as well as the crystal plane contained in the film are not known. The use of the polarized light was, however, decisive to resolve the factor group splitting components in the spectrum of form IV.

A first point of interest in the vibrational assignment concerns the ν_{20} fundamental. In fact, some authors locate ν_{20} at 820 cm^{-1} following a suggestion of Waddington *et al.*[1] who proposed this value in order to fit

TABLE I Infrared and Raman spectra of crystalline thiophene†

FORM I (T = 180 K)		FORM II (T = 150 K)		FORM III (T = 77 K)					FORM IV (T = 77 K)					
Infrared	Raman	Infrared	Raman	Infrared				Raman	Infrared				Raman	Assignment
random				Random	Oriented	α	β		Random	Oriented	α	β		
450.4 w	454 w	452.8 sh 453.8 w	452.5 sh 455 w	450.8 w 453.6 w 456.0 sh	451.2 453.6 455.3	w vw —	-- m sh	453 w 455 sh 458 w	453.5 m 456.4 sh	453.5 455.0 456.4	w sh sh	w sh sh	454 w 456 sh	$\nu_{21}(B_2)$
—	—	--	—	—	—	—	—	—	566.6 vw	—	—	—	—	$^{13}C\ \nu_{11}(A_2)$
569 vw	568 vw	—	566 w 569 sh	567.0 vw 570.0 vw 572.4 vw	—	—	—	563 sh 566 w 571 w	570.0 vw 573.2 vw 576.0 vw	—	—	—	565 w 571 vw	$\nu_{11}(A_2)$
—	—	--	596 vw	—	—	--	—	597 vw	—	—	—	—	597 vw	$^{13}C\ \nu_8(A_1)$
—	—	—	—	602 sh	—	—	—	603 sh	—	—	—	—	—	$^{34}S\ \nu_8(A_1)$
606 vw	606 s	604.0 sh 608.0 w	606 s	604 sh 605.6 sh 606.8 w	606.8	—	w	605 m 608 sh	606.4 sh 608.4 vw	—	—	—	605 s 608 sh	$\nu_8(A_1)$
694 sh	689 vw	708 vw	695 vw 709 vw	695.2 vw 704.0 vw 706.8 vw	695.2 704.0 706.0			689 vw 696 vw 705 vvw	703.6 vw	702.8 708.2	w	—	689 w 695 vw 703 vvw 710 vvw	$\nu_{10}(A_2)$
719.0 vs 721 sh	—	712.4 s 719.0 s	—	714 vs 720 vs	714 721	vs —	— vs	715 vw	714 vs 718.4 vs 720.8 sh	714 718.8 720.4	vs — sh	— vs sh	—	$\nu_{19}(B_2)$
—	—	724.8 sh	—	724 sh	724	—	sh	—	724 sh	725	-	sh	—	
—	—	—	—	—	—	—	--	—	—	734.8	sh	sh	—	
—	—	—	—	739 sh	739.4	w	—	—	738 w	739	—	w	—	
—	—	—	—	—	—	—	—	740 vvw	—	—	—	—	739 vvw	$^{13}C\ \nu_{18}(B_1)$
—	—	—	746 sh	744 vvw	—	—	—	745 sh	—	—	—	—	745 sh	$^{34}S\ \nu_{18}(B_1)$
749 w	749.5 m	748.6 w	749 m 751.5 sh	749.2 w 750 w 750.8 sh	749.2 749.8 750.8	sh w —	sh — w	748 m 750.5 sh	748.4 sh 750.4 w	747.4 750.4	— w	vw w	749 m	$\nu_{18}(B_1)$
820 vw	820 vw	818 vw	—	819 vw	—	—	—	821 vw	820 vw	—	—	—	821 vw	$^{13}C\ \nu_3(A_1)$

TABLE I (*continued*)

FORM I (T = 180 K)		FORM II (T = 150 K)		FORM III (T = 77 K)					FORM IV (T = 77 K)					
Infrared	Raman	Infrared	Raman	Infrared				Raman	Infrared				Raman	Assignment
random				Random	Oriented	α	β		Random	Oriented	α	β		
832 sh 833.6 s	833.5 vs	830.8 vs 834.4 sh	832 vs 833.5 sh	830 sh 832 vs 835 sh	829.6 831.6 835.0	s sh s	— s sh	829 sh 832 vs 835 vs	827 sh 831.2 vs 835 sh	827 831.2 835	— s sh	w sh w	827 m 833 sh 836 s	$\nu_3(A_1)$
—	—	—	—	864 vvw	—	—	—	—	864 vvw	—	—	—	—	
870 vw 873 sh	871 w 876 w	868.8 w 869.6 sh 876 w	870 w 881.5 vw	869.2 w 871.2 w 872 sh 880.2 vw 883 vw	869 871 880.4	w w w	— — —	871 w 872 sh 876 vw 883 vvw	869.0 w 870 w 874.8 w 881 sh	869.2 870.4 874.4	sh — —	sh w vw	871 w 876 w 881 sh 886 sh	$\nu_{17}(B_1)$ and $\nu_{20}(B_2)$
—	—	906 vw	905 vw	905.8 w 907.6 sh	906	vw	vw	906 vw	906 w	905	vw	vw	906 w 908 sh	$2\nu_{21}$
911 vw	912 vw	914 vw	—	913.6 vw 916.4 vw	914 917	— vw	vw vw	915.5 w	912 sh 919 w 922.8 sh	912 919 923	— — sh	vw w sh	916 w	$\nu_9(A_2)$
—	—	—	—	—	—	—	—	—	1015 vvw	—	—	—	—	$\nu_{11} + \nu_{21}$
1023 w	*1025 w*	*1022.5 w*	*1022.5 w*	*1020 w*	*1021.5*	vw	vw	*1021 w*	*1022 w*	*1023*	vw	vw	*1023.5 w*	$^{13}C\ \nu_7(A_1)$
1032 m	1031 vs	1032.5 sh	1031.5 s 1033.5 sh	1028.5 m 1029.5 sh 1031.5 m	1029 1030 1031.5	m — w	— m —	1029 s 1031 sh 1032 sh	1029 m 1030.5 sh 1033 sh	1029 1031.5 1032.5	sh w —	sh — sh	1031.5 s 1032.5 sh	$\nu_7(A_1)$
—	—	1033.5 m	—	1033.5 sh	1034	sh	—	—	1038 vw	1038	vw	vw	—	$\nu_8 + \nu_{21}$
1078.5 m	1079 s 1084 sh	1075 m 1078 m 1084 m 1085.5 sh 1089 sh	1079.5 s 1085 sh 1091 sh	1074.5 s 1078.5 s 1082 sh 1083.5 s 1086 s 1088 s	1074.5 1078.5 1082 1083.5 1086 1088.5	m w — m — w	vw — s m w —	1076 s 1077.5 sh 1081.5 sh 1083.5 m 1086 m 1088.5 m	1074 m 1076 sh 1081.5 m 1085.5 m	1074 1075.5 1077.5 1080.5 1081.5 1086	m sh — — — vw	sh — w sh m m	1076.5 m 1080 m 1087.5 m 1088.5 sh	$\nu_6(A_1)$ and $\nu_{16}(B_1)$

1245 w	—	1244 w	—	1242 w 1243 w 1244 w	1242 1243 1244	vw w —	— — w	—	1243 w	1243	vw	vw	—	^{13}C $\nu_{15}(B_1)^a$
1250 s	—	1249.5 s 1251 s	1250 vw	1248 s 1250 s 1251 sh	1248.5 1249 1251	s — sh	— s sh	1249 w 1252 sh	1248 s 1251 s	1247.7 1248.5 1251	s — sh	— s s	1251 vw	$\nu_{15}(B_1)$
—	—	—	1349 w	—	—	—	—	1348 w	—	—	—	—	1348.5 w	^{13}C $\nu_4(A_1)^b$
—	—	—	—	1353.5 vw	—	—	—	—	1353 vvw	—	—	—	1354.5 sh	$\nu_8 + \nu_{18}$
—	—	—	—	1356.5 vw	1356.5	vw	—	1357 sh	—	—	—	—	—	^{13}C $\nu_4(A_1)^a$
1358 vw	1358 vw	1359 sh 1361 vw	1362 s	1360 sh 1361.2 w	1360.5 1361.2	w —	— w	1360 s 1362 s	1358 w 1360.5 w	—	—	—	1359 m 1361.5 m	$\nu_4(A_1)$
—	—	—	—	1376 vw	—	—	—	1377 vw	1377 vw	—	—	—	1378 vw	
—	—	—	—	1386.5 sh	—	—	—	1387.5 sh	—	—	—	—	—	^{13}C $\nu_5(A_1)^b$
1408 m	1404 sh 1408.5 s	1408 m	1409 m	1405 sh 1408.5 m	1404 1408 1411	— m sh	w — —	1404 sh 1409 m	1408.5 m 1410 sh	1408 1410	w —	— m	1406 sh 1410 m	$\nu_5(A_1)$
—	—	1420 br	—	1424 br	—	—	—	—	1425 br	—	—	—	—	$2\nu_{19}$
—	—	—	—	1433.5 sh	—	—	—	—	—	—	—	—	—	$\nu_8 + \nu_3$
—	—	—	—	1454 sh	—	—	—	—	—	—	—	—	—	$\nu_9 + \nu_{21}$
1503 w	1503 w	1503 w 1505 w	1504.5 vw	1501 sh 1502.5 w 1504.5 sh	1501 1502.5 1504	sh w —	sh w sh	1503 w	1502 sh 1504 w	1501.5 1502.5 1504.5	sh — w	sh w —	1502 vw	$\nu_{14}(B_1)$
3076 sh	3070 vw	3071 w	3070 m	3066 w 3071 vw	—	—	—	3066 m 3067 sh	3073 vw	—	—	—	3068 m	$\nu_{13}(B_1)$
3082 w	3078 w	3080 w	3081 m	3076 sh 3078 w 3081 w	—	—	—	3077.5 m 3081 m	3078 w	—	—	—	3078 m	$\nu_2(A_1)$
3102 m	3105 w	3100 s 3102 sh	3104 s 3106 sh	3096 sh 3101 s	—	—	—	3101 s	3099 m 3104 sh	—	—	—	3102 sh 3106 s	$\nu_1(A_1)$
—	—	—	—	3108 w 3111 w	—	—	—	3108 m 3112 m	3112 vw	—	—	—	3112.5 m	$\nu_{12}(B_1)$

† Frequencies in cm^{-1} units; vs = very strong, s = strong, m = medium, w = weak, vw = very weak, sh = shoulder, br = broad, α, β is polarization of the infrared bands (see text). a, b denote the alpha and beta positions of the ring.

the experimental heat capacity data, some others at 870 cm^{-1}, very close to ν_7, on the basis of the isotopic product rule. Since in the infrared spectrum of form III we observe six absorption peaks in the 890–860 cm^{-1} region, two close lying fundamentals must occur in this region. We conclude therefore that the second assignment is the correct one, in agreement with the gas phase assignment.

Furthermore, in order to distinguish in the crystal spectrum isotopic peaks from the splitting components, we have carried out a calculation of the isotopic normal frequencies for the free molecule on the basis of the valence force field reported in Ref. 12. It may be expected that the isotopic frequency shifts in the crystal should be about the same as in the gas phase since the static crystal field affects the vibrational frequencies of the light and isotopic molecules to the same extent. As shown in Table I, it has been possible to identify as isotopic peaks several weak bands which appear on the low frequency side of the fundamentals. Moreover, for vibrations involving specifically the motion of the carbon atoms (ν_{15}, ν_{11} and ν_5), we were able to distinguish among the peaks due to molecules containing ^{13}C in the α or in the β position of the thiophene ring.

CRYSTAL FORMS

The infrared and Raman spectra of polycrystalline thiophene at various temperatures are shown in Figures 1 and 2 respectively. Infrared spectra in polarized light of oriented films of forms III and IV at 77 K are reported in Figure 3. The full line spectra refer to a polarizer-sample orientation corresponding to the highest intensity of the peak at about 1074 cm^{-1} and will be referred to as α spectra. The dotted line spectra were obtained with a 90° rotation of the polarizer and will be indicated as β spectra. Figure 4 shows the Raman spectrum of all the phases in the lattice region.

Form I is stable from the melting point (235 K) to 171.6 K and was obtained only by crystallization of a liquid film. Its crystal structure has been investigated by X-ray crystallography[6] and it has been found to be orthorhombic, space group D_{2h}^{18} or C_{2v}^{17} with four molecules in the unit cell. A definite choice of the space group is made difficult by the presence in the crystal of orientational disorder which arises from the fact that molecules located on the same site can assume different orientations with respect to the normal to the molecular ring. Of course, also the infrared and Raman spectra are affected by this orientational disorder and generally show broad bands with unresolved fine structure. In the Raman spectrum only two very broad lattice modes are observed at about 55 and 112 cm^{-1} (Table II).

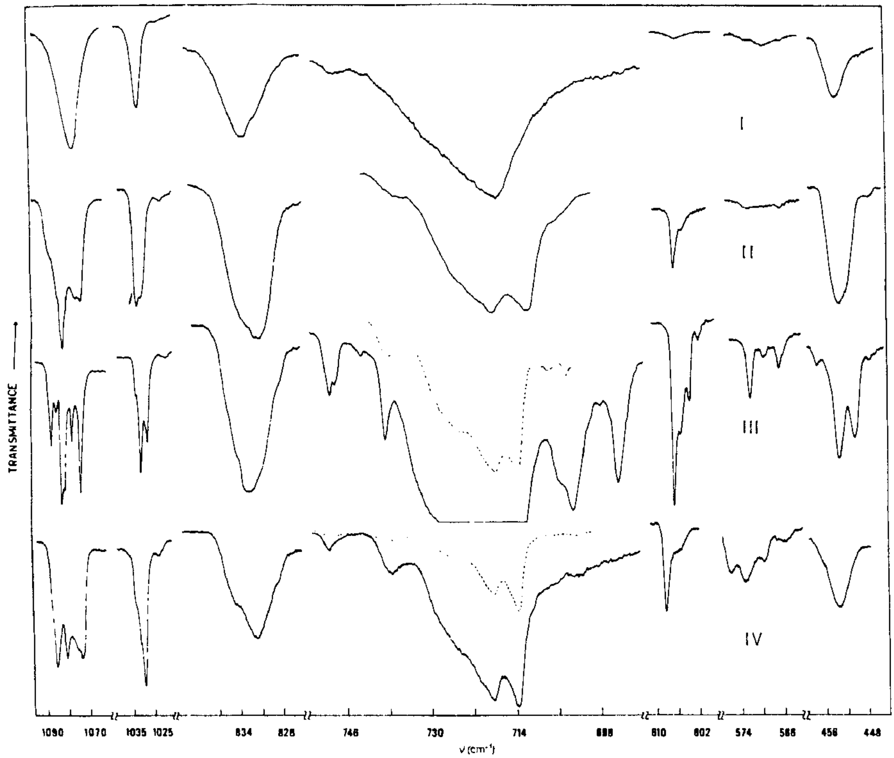

FIGURE 1 Infrared spectra of the four solid phases of thiophene (random samples). The spectra were registered at 188 K (I), 153 K (II) and 77 K (III and IV). Dotted line spectrum refers to a thinner sample.

From the foregoing it is clear that the vibrational data do not give additional help in the elucidation of the crystal structure.

Form II exists in a temperature range between 171.6 K and 138 K and can be obtained either by cooling the liquid film or by annealing crystalline samples of form IV.

Concerning this form we were able to observe only some spectroscopic features which however were not sufficient for a detailed vibrational analysis of the crystal.

The most important spectral features are:

a) Activity of all the expected fundamentals in the infrared spectrum. This means that the site symmetry is lower than the C_{2v} molecular symmetry.

b) Most of the bands show splitting into two components. Infrared and Raman frequencies are generally coincident.

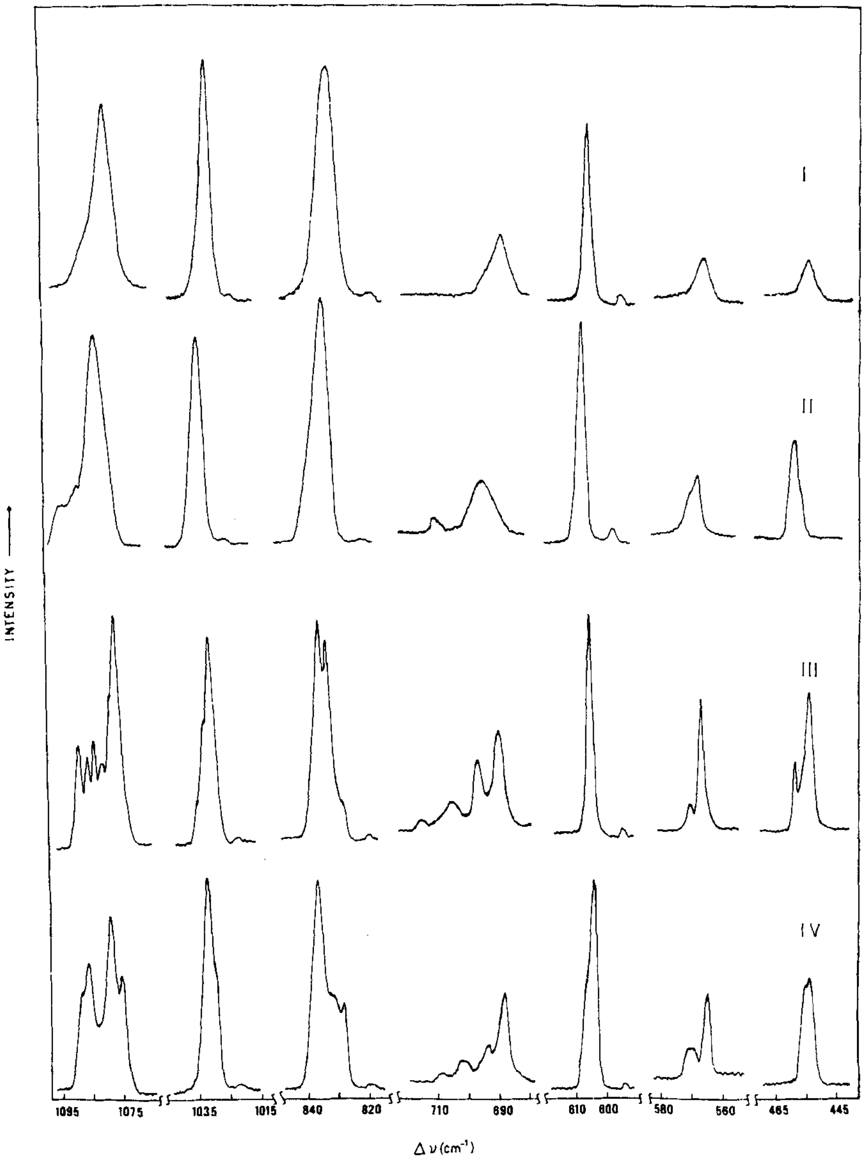

FIGURE 2 Raman spectra of the four solid phases of polycrystalline thiophene registered at 188 K (I), 153 K (II) and 77 K (III and IV).

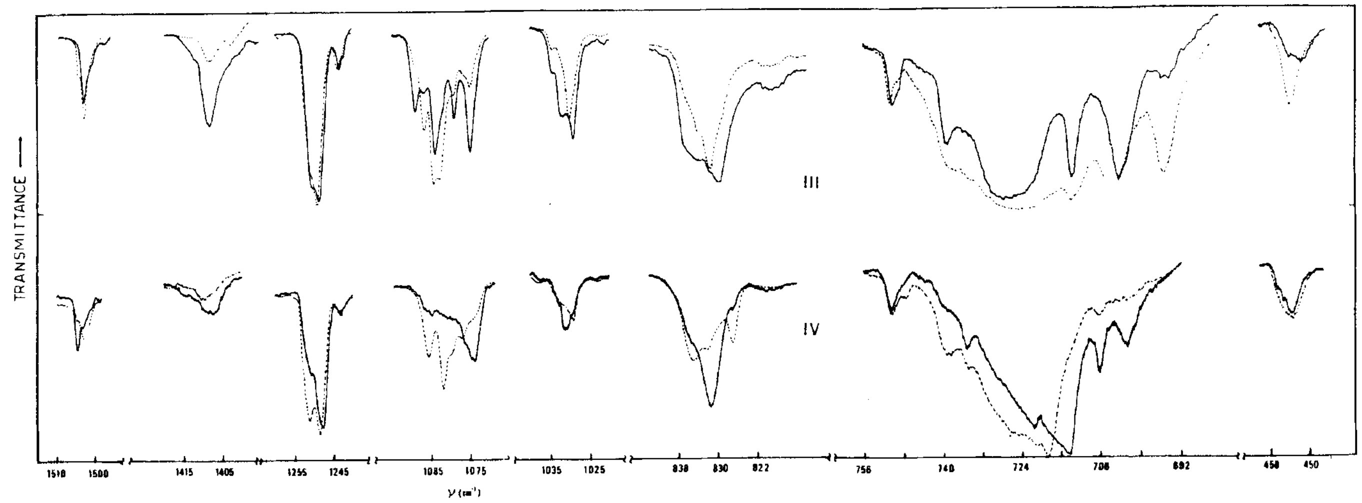

FIGURE 3 Infrared absorptions of crystalline thiophene. Spectra in polarized light of oriented films of form III and IV at 77 K. Full line, α polarized; dotted line, β polarized. For the meaning of α and β, see text.

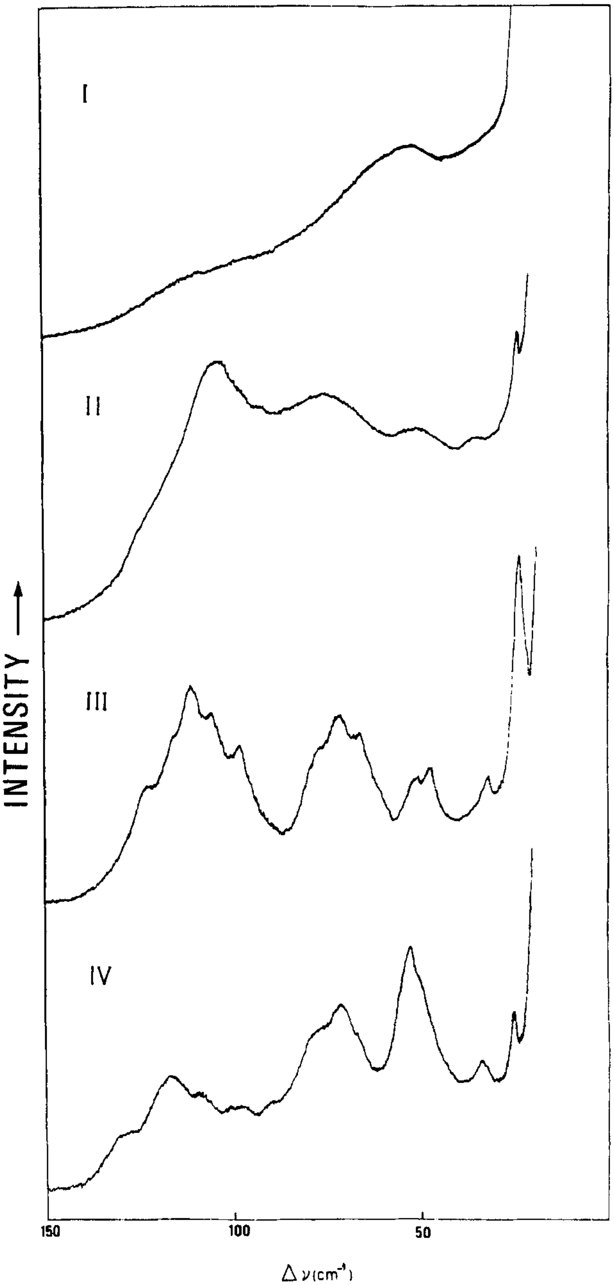

FIGURE 4 Low frequency Raman spectrum of solid thiophene at 188 K (I), 153 K (II) and 77 K (III and IV).

TABLE II Raman lattice modes of crystalline thiophene†

Form I (T = 180 K)		Form II (T = 150 K)		Form III (T = 77 K)		Form IV (T = 77 K)	
ν	I	ν	I	ν	I	ν	I
55	m	26	w	26	s	26	m
112	br	36	br	34	m	35	w
		52	m	49	m	44	w
		76	br	53	m	50	sh
		92	w	61	sh	53	s
		103	s	67	s	68	sh
		117	sh	73	s	72	s
				78	s	79	m
				100	m	90	w
				107	s	100	br
				113	s	110	s
				116	sh	117	m
				124	m	129	m

† Frequencies in cm^{-1} units; s = strong, m = medium, w = weak, br = broad, sh = shoulder.

c) A close similarity between the band shape of the spectra of forms II and III. This fact suggests that minor differences exist in their crystal structures.

Form III is always obtained from the second one by lowering the temperature below 138 K. By a further cooling it does not transform anymore and can be isolated as a metastable form at 77 K.

The analysis of the vibrational spectra allowed us to establish that:

a) All the expected fundamentals are infrared active and, in general, split into three components.

b) The same multiplicity is shown by most of the Raman bands. Coincidence is observed between the infrared and Raman splitting components. Thirteen peaks occur in the Raman lattice region.

These results strictly support the presence of a non-centrosymmetric orthorhombic crystal structure with four molecules in general position. However, a choice between C_{2v} and D_2 factor group is practically impossible, the only criterion being the coincidence or not of the totally symmetric Raman splitting component with an infrared peak.

Form IV, stable below 112 K, was isolated either by a fast cooling starting from form I or by annealing the glassy samples obtained by vapor deposition at 77 K.

From the inspection of the spectra we note:

a) The infrared and Raman bands are in general broader and show a less resolved fine structure than those of form III.

b) Most of the Raman bands split into two components, apart from the ν_3 and ν_{10} which show a triplet and quartet structure, respectively. In the Raman spectrum thirteen lattice modes are detected.

c) In the infrared spectrum in polarized light three components are observed for most of the fundamentals.

All these data together with the coincidence between the frequencies of the infrared and Raman splitting components lead also for this phase to the same conclusions above proposed for form III (i.e. site symmetry C_1, factor group D_2 or C_{2v}).

Finally we emphasize that, for this phase, the use of the polarized light on oriented samples has been determinant for the identification of all the infrared splitting components.

CONCLUSIONS

At first most of our attention in studying the phase transitions in crystalline thiophene was devoted to the identification of each crystal form by means of vibrational spectroscopy. We succeeded in isolating the first three forms by following the indications given by the heat capacity measurements whereas we were not able to induce the III → IV phase transition and vice versa. Form IV was instead obtained by a fast cooling of form I. Its infrared spectrum compares well with those reported in the literature and attributed to form IV.

At this point we wish to remark that, even if the spectroscopic identification of forms III and IV cannot be questioned on the basis of the arguments presented above, the infrared spectrum of form III, which shows bands with a great sharpness and a well resolved fine structure, seems in better agreement with the occurrence of a more ordered crystal structure usually consistent with the lowest temperature stable form.

Concerning with the mechanism involved in the phase transitions, the first order I → II phase transition is of disorder-order type and probably consists in the freezing of the molecules in a unique orientation. This is supported by the vibrational spectrum of form II which shows a sufficiently resolved fine structure of the bands in accordance with an ordered arrangement of the molecules in the crystal.

The other two phase transitions, of lambda type, involve only a small amount of energy. From the spectroscopic data it results that they do not affect either the crystalline system or the site symmetry. In particular, if we consider that the vibrational spectrum of form III closely resembles that of form II, it seems reasonable to suppose that the II → III phase transition is related only with a rearrangement of the molecules in the unit cell without the site and the factor group symmetries being affected.

As to the form IV, its crystal structure should differ substantially from that of the phase III, as shown by the completely different pattern exhibited in the lattice Raman region. Therefore it is possible that a change in the factor group symmetry occurs (from C_{2v} to D_2 or vice versa) going from form III to form IV, whereas it is well established that the site symmetry as well as the number of molecules in the unit cell remain unchanged.

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