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## Dynamics of polythiophene

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**Abstract.** It is well known that defects play a central role in the values of the transport properties of the conducting polymers. With the aim of determining the nature of these defects in polythiophene, the dynamics of this compound are investigated. In this paper, results concerning the first-order and second-order infrared absorption spectra of a finite and infinite chain are reported. The calculated values of the frequencies of active vibrational modes (infrared and Raman) are in very good agreement with experimental data for the hydrogenated and the deuterated polymers. This analysis enabled us to determine the frequencies of peaks which are most probably due to the presence of defects.

### 1. Introduction

Polythiophene (PT) belongs to a class of organic polymers that show interesting conducting properties after doping (Kaneto *et al* 1983, Tourillon and Garnier 1983). In the same way as polypyrrole and poly-p-phenylene, PT presents a non-degenerate ground state and, as a result, polarons and bipolarons are expected to be the dominant charged species which appear on the polymer chain upon doping (Kaneto *et al* 1984, Bredas *et al* 1984, Bertho and Jouanin 1987, Bertho *et al* 1988). Recently various studies of PT have been published (Kaneto and Yoshino 1987, Vardeny *et al* 1987). Moreover the crystal structure of thiophene-based conducting polymers is not exactly resolved at present (Tourillon and Garnier 1985, Garnier *et al* 1985, Mo *et al* 1985). For the chain, several configurations are possible. Recent x-ray and spectroscopic results show that the structure reported in figure 1 is the most probable (Mo *et al* 1985, Bredas and Chance 1982).

The aim of this study is to investigate the dynamics of perfect chain and chains with defects; it has been conducted with the purpose of determining the nature of the defects and their effects on the conductivity of polythiophene. In this paper, we study the in-plane properties of the perfect infinite and finite chain and we determine the parameters of the force field so that the infrared and Raman spectra of PT (hydrogenated as well as deuterated) are fully analysed.

Then, in the following, we report in § 2 the available experimental data concerning the infrared and Raman spectra of PT (hydrogenated and deuterated). In § 3, we present a group theory analysis. The force field model is described in § 4. The results for infinite and finite chains are reported in § 5 where discussion and comparison with experiments are developed.

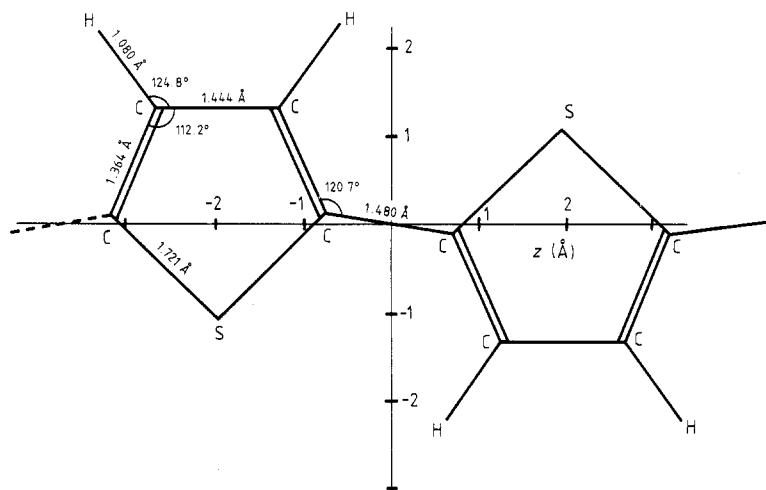


Figure 1. Structure of the PT unit cell.

Table 1. Infrared data from Furukawa *et al* (1987).

Wavenumber ( $\text{cm}^{-1}$ )						
2T	3T	4T	6T	PT	PTC	PTD
695	676 688	688 702	685 700	695	695	524
Doublet near 810	798 + 1 line	798 + 1 line	790 + 1 line	786 + 1 line	786	621
1417	1424	1425	1426	1440	1427	1420
1442	1460	1449	1443 1456	1457		
1499	1497	1493	1493	1490	1475	1443

Table 2. Raman data from Furukawa *et al* (1987).

Wavenumber ( $\text{cm}^{-1}$ )						
2T	3T	4T	6T	PT	PTC	PTD
676	691	694		652 682 701	646 677 697	641 668 686
1047 1079	1051	1054	1053	1045	1041	778
	1224	1225		1155 1177 1222	1130 1154 1191	1214
1444	1461	1463	1460 1456	1461	1427	1440
1556	1530	1519	1507	1498	1484	1464

**Table 3.** Data for PT and PTD from Lere-Porte *et al* (1988) and Hasoon *et al* (1989) with our present proposed assignment. The asterisks indicate in-plane PT or PTD modes.

Infrared		Raman	
Wavenumber (cm <sup>-1</sup> )	Mode	Wavenumber (cm <sup>-1</sup> )	Mode
PT			
452	Out of plane	647	*
520	Combination	682	Chain end?
580	*	702	Out of plane
695	* (+ chain end)	741	*
714	Out of plane?	1045	*
739	*	1152	Defects?
785	Out of plane	1171	*
825	*	1220	*
846	Defects	1458	*
1040	*	1476	*
1140	Defects	1500	* (+ defects)
1203	Defects	2900	Harmonic
1225	*	2950	Harmonic
1341	Defects		
1356	*		
1439	*		
1492	* (+ combination and defects)		
2200–2300	Combinations		
2316 <sup>a</sup>	Defects		
3063	*		
3100	*		
PTD			
455	Out of plane	640	*
516	Combination	669	Out of plane
587	*	690	*
602	Chain end	753	*
622	Out of plane	780	Defects?
643	Out of plane	860	Defects?
673	*	985	*
699	*	1128	Defects?
754	*	1205	*
826	*	1290	Defects?
846	Defects	1432	*
974	*	1459	*
1024	Defects	1500	Defects
1205	Defects		
1280	*		
1421	*		
1446	*		
1500	Defects		
2282	*		
2300	*		

<sup>a</sup> In poly(2,5-deuteriothiophene).

## 2. Experimental data

The available experimental data have been reported in tables 1–3. Furukawa *et al* (1987) analysed their infrared and Raman spectra for the hydrogenated polymer PT (tables 1 and 2) on the basis of data of the oligomers,  $\alpha$ -bithiophene ( $\alpha$ -2T),  $\alpha$ -terthiophene ( $\alpha$ -3T),  $\alpha$ -quaterthiophene ( $\alpha$ -4T) and  $\alpha$ -sexithiophene ( $\alpha$ -6T). They obtained the degree of polymerisation, the average number of *s-trans* conjugate successive rings and the amount of the distorted part relative to the conjugated part. They also supplied results concerning  $^{13}\text{C}$ -PT (PTC) and deuterated PT (PTD). An interesting result of these experiments reported in tables 1 and 2 is the dependence of the frequency of infrared- and Raman-active modes on the length of the chain. In fact, a correlation between the frequency shift and the length of the chain is clearly apparent. Only the Raman-active mode at  $1498\text{ cm}^{-1}$  for PT shows a large decrease with increasing length. However, this mode is found at  $1511\text{ cm}^{-1}$  in thiophene; so we cannot conclude a simple dependence with any certainty. Vardeny *et al* (1987) have shown that the resonant Raman scattering spectrum of PT exhibits a line at around  $1500\text{ cm}^{-1}$  which depends strongly upon the wavelength of the laser excitation. So it is possible to attribute this to a defect mode which overlaps a normal mode of the lattice. This defect mode is also observed in PTD.

All these results enable us to conclude that atom–atom interactions mediated via electron–phonon coupling do not present a long-range character.

Österholm *et al* (1987) obtained absorption bands in the  $3000\text{--}3100\text{ cm}^{-1}$  region, in contrast with the results of Tourillon and Garnier (1983, 1985); they conclude that the dominating tendency of the thiophene is to form a corresponding polymer PT via 2–5 coupling. Taliani *et al* (1987) studied both neutral and doped PT. Cao *et al* (1987) found that four modes appear at  $1030$ ,  $1100$ ,  $1200$  and  $1330\text{ cm}^{-1}$  when PT is doped.

Very recently, careful Raman scattering and infrared optical absorption measurements have been performed by Lere-Porte *et al* (1988) and by Hasoon *et al* (1989). Hasoon (1988) also performed a group analysis of PT. All these last experimental measurements are shown in table 3 for PT and PTD. To show the correspondence between the data obtained for thiophene and PT, the fundamental modes of thiophene (Scott 1969) are reported in table 4. Comparison of the spectra of the monomer and polymer allowed Hasoon (1988) to perform the first assignment of the active vibrational modes of hydrogenated PT.

**Table 4.** Fundamental frequencies of thiophene from Scott (1969).

Fundamental frequency ( $\text{cm}^{-1}$ )			
$A_1$ modes	$B_1$ modes	$A_2$ modes	$B_2$ modes
608	751	567	452
839	872	688	712
1036	—	898	867
1083	1256		
1360	1503		
1409	3086		
3098	—		
3126			

### 3. Group theory analysis

We consider, in the following, only the in-plane vibrations. First we consider the case of thiophene. PT will be considered later.

#### 3.1. Thiophene

The structure of thiophene  $C_4SH_4$  (Cyvin and Cyvin 1969) is reported in figure 2.

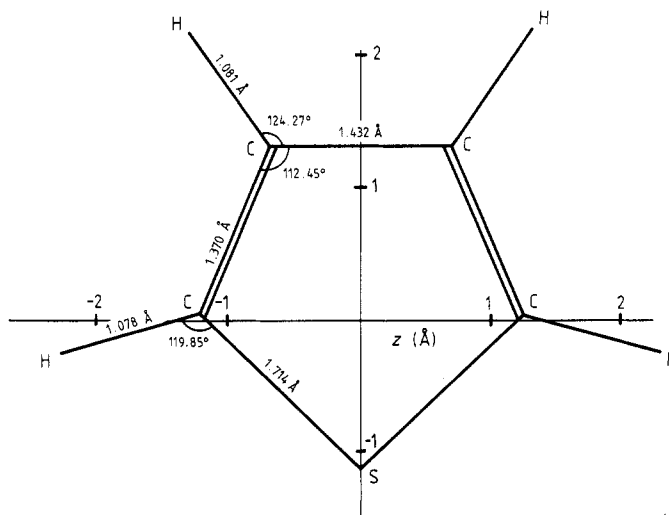


Figure 2. Structure of thiophene.

Molecular vibrational analysis has been reported by Bolotina and Sverdlov (1967). The  $C_{2v}$  group analysis is reported in table 5. There are, in plane, 18 degrees of freedom corresponding to 15 vibrational modes.

The decomposition of the in-plane motion gives  $\Gamma = 9A_1 \oplus 9B_1$ ; it corresponds to eight vibrations  $A_1$ , seven vibrations  $B_1$  plus two translations  $A_1$  and  $B_1$  and one rotation  $B_1$ .

The  $A_1$  modes are isotropic Raman active, the  $A_1$  and  $B_1$  modes are anisotropic Raman active, while the  $A_1$  and  $B_1$  modes are infrared active.

Table 5. Irreducible representations for the thiophene point group  $C_{2v}$ .

$C_{2v}$	E	$C_{2z}$	$\sigma_y$	$\sigma_z$	Translation, rotation
$A_1$	1	1	1	1	$T_x$
$A_2$	1	1	-1	-1	$R_x$
$B_1$	1	-1	1	-1	$T_z, R_y$
$B_2$	1	-1	-1	1	$T_y, R_z$

Table 6. Irreducible representations for the PT point group  $D_{3h}^5$  at the  $\Gamma$  and  $Z$  points.

	E (0, 0, 0)	$C_{2x}$ (0, 0, c/2)	$C_{2y}$ (0, 0, 0)	$C_{2z}$ (0, 0, c/2)	I (0, 0, 0)	$\sigma_x$ (0, 0, c/2)	$\sigma_y$ (0, 0, 0)	$\sigma_z$ (0, 0, c/2)	Translation, rotation
$\Gamma$ point									
$\Gamma_1 A_g$	1	1	1	1	1	1	1	1	
$\Gamma_2 A_u$	1	1	1	1	-1	-1	-1	-1	
$\Gamma_3 B_{2g}$	1	1	-1	-1	1	1	-1	-1	$R_x$
$\Gamma_4 B_{3u}$	1	1	-1	-1	-1	-1	1	1	$T_x$
$\Gamma_5 B_{2g}$	1	-1	1	-1	1	-1	-1	-1	$R_y$
$\Gamma_6 B_{2u}$	1	-1	1	-1	-1	1	1	1	$T_y$
$\Gamma_7 B_{1g}$	1	-1	-1	1	1	-1	-1	1	$R_z$
$\Gamma_8 B_{1u}$	1	-1	-1	1	-1	1	-1	-1	$T_z$
Z point									
$Z_1$	2	0	0	0	0	0	2	0	
$Z_2$	2	0	0	0	0	0	-2	0	

### 3.2. Polythiophene

The structure of PT is reported in figure 1. The unit cell contains 14 atoms. The space group of the chain is isomorphic to the factor group  $m\bar{c}m$  with the subgroup of translation perpendicular to the chain. The tables of Kovalev (1965) give the character of the irreducible representations for this group  $D_{2h}^5$ .

Table 6 gives the irreducible representations of the group at the  $\Gamma$  point ( $\mathbf{k} = (0, 0, 0)$ ) and at the  $Z$  point ( $\mathbf{k} = (0, 0, \pm c/2)$ ). There are, in plane, at the  $\Gamma$  point, 28 degrees of freedom corresponding to 26 vibrational modes.

The decomposition of the representation given by the in-plane motion into irreducible representations is (for the  $\Gamma$  point)  $\Gamma = 7\Gamma_1 \oplus 7\Gamma_4 \oplus 7\Gamma_5 \oplus 7\Gamma_8$ ; it corresponds in the usual spectroscopic notation to seven vibrations  $A_{1g}$ , six vibrations  $B_{3u}$ , seven vibrations  $B_{2g}$ , six vibrations  $B_{1u}$  plus two translations  $B_{3u}$  and  $B_{1u}$ . For the  $Z$  point the decomposition gives  $Z = 14Z_1$ ; it corresponds to 14 doubly degenerate vibrations of the same symmetry.

The representation given by the photon operator is  $\Gamma_4 \oplus \Gamma_6 \oplus \Gamma_8$ . Only vibrations which give one of these representations will be active in one-phonon process infrared absorption ( $B_{3u}$  and  $B_{1u}$  in plane, and  $B_{2u}$  out of plane).

The representation given by Raman scattering operator is  $\Gamma_1 \oplus \Gamma_3 \oplus \Gamma_5 \oplus \Gamma_7$ . Only vibrations which give one of these representations will be active in one-phonon Raman scattering ( $A_{1g}$  and  $B_{2g}$  in plane, and  $B_{1g}$  and  $B_{3g}$  out of plane).

The group correlations between thiophene and PT are summarised in table 7 using the usual spectroscopic notation for representations. These correspondences have been used by Hasoon (1988) to give a first assignment of PT lines reported here in table 3 by comparison with the lines of thiophene reported here in table 4.

**Table 7.** Correlations between irreducible representations for thiophene and PT (at the  $\Gamma$  point) groups.

$C_{2v}$	$D_{2h}^5$ at the $\Gamma$ point
$A_1$	$A_g, B_{3u}$
$A_2$	$B_{3g}, A_u$
$B_1$	$B_{2g}, B_{1u}$
$B_2$	$B_{1g}, B_{2u}$

## 4. Model

Two structures have been proposed for  $\alpha$ -PT. Recent x-ray studies show that the structure reported in figure 1 is certainly the most probable. It is well known (Mele and Rice 1980) that electron-phonon interactions can give significant contributions to inter-atomic force constants, leading to rather long-range effects. However, the existence of a very good force field model for thiophene (Scott 1969) and the weak dependence of the frequency of modes on the length of the chain show that the effects of electron-phonon coupling can certainly be included in the phenomenological force constants of a force-field model.

We start with a general expansion of harmonic potential energy in terms of the internal coordinates of the chain (34 for the unit cell). In the same manner as Scott (1969) did for thiophene, we retain only the main interaction terms. In all, there are 40 possible



**Table 8.** Comparison of calculated PT and PTD vibrational mode wavenumbers and experimental values. The  $\nu_{\text{obs}}$ -values for the Raman bands were taken from the work of Lere-Porte *et al.* (1988), and the  $\nu_{\text{obs}}$ -values for the infrared absorption bands from the work of Hasoon *et al.* (1989).

Calculated first-order Raman scattering bands				Calculated infrared absorption bands			
A <sub>g</sub> modes (isotropic Raman active)		B <sub>2g</sub> modes (anisotropic Raman active)		B <sub>1u</sub> modes (infrared active along O <sub>z</sub> )		B <sub>3u</sub> modes (infrared active along O <sub>x</sub> )	
$\nu_{\text{cal}}$ (cm <sup>-1</sup> )	$\nu_{\text{obs}}$ (cm <sup>-1</sup> )	$\nu_{\text{cal}}$ (cm <sup>-1</sup> )	$\nu_{\text{obs}}$ (cm <sup>-1</sup> )	$\nu_{\text{cal}}$ (cm <sup>-1</sup> )	$\nu_{\text{obs}}$ (cm <sup>-1</sup> )	$\nu_{\text{cal}}$ (cm <sup>-1</sup> )	$\nu_{\text{obs}}$ (cm <sup>-1</sup> )
PT							
323	—	315	—	239	—	585	580
650	647	510	—	693	695	826	825
1043	1045	738	741	732	739	1041	1040
1225	1220	1168	1171	1227	1225	1352	1356
1461	1458	1296	—	1495	1492	1431	1439
1477	1476	1498	1500	3071	3063	3084	3100
3085	—	3071	—	—	—	—	—
PTD							
320	—	308	—	228	—	581	587
637	640	480	—	675	673	752	754
755	753	692	690	706	699	824	826
1201	1205	988	985	966	974	1284	1280
1431	1432	1229	—	1447	1446	1426	1421
1460	1459	1457	1459	2279	2282	2310	2300
2312	—	2279	—	—	—	—	—

independent parameters which are given in table 9 later. To determine these constants, we use the usual non-linear least-squares fitting procedure in such a way as to reduce as much as possible the number of force constants (cancellation of parameters which are not really significant and setting to thiophene values when possible). The iterative process is stopped when the RMS between calculated and observed mode wavenumbers is a minimum (near the experimental accuracy).

The dynamical matrix  $\mathbf{D}$  is obtained from

$$\mathbf{D} = \mathbf{M}^{-1} \mathbf{U}^{-1} \mathbf{V} \mathbf{U} \mathbf{M}^{-1}$$

where  $\mathbf{V}$  is the matrix of potential written in terms of the internal coordinates,  $\mathbf{U}$  is the matrix of coordinate change from internal to Cartesian coordinates and  $\mathbf{M}$  is a diagonal matrix with elements equal to inverse of square root of atomic masses.

In order to study the dynamical properties of systems with any kinds of defect, the matrix  $\mathbf{U}$  is directly computed for a general structure. The values of force constants are determined for the infinite chain.

## 5. Results

The results have been obtained mainly with an infinite-chain model.

### 5.1. Frequencies

For fitting procedures we have used the experimental data of Lere-Porte *et al* (1988) for the Raman-active modes and those of Hasoon *et al* (1989) for the infrared-active modes. These data are actually the most complete and accurate.

In table 8, experimental infrared and Raman modes are compared with calculated modes for PT and PTD. The agreement is rather good. The calculated standard deviation is  $5.3 \text{ cm}^{-1}$  for the 19 assigned bands of PT and  $4.3$  for the 19 assigned bands of PTD.

Table 9 gives the values of the 40 force constants deduced from the fit: of these, five are fixed to their value for thiophene and three are cancelled; the remaining 32 constants are adjusted in order to fit the 38 observed modes. The significance of these parameters is given in the last digit; it corresponds to a maximum variation in calculated frequencies equal to the experimental accuracy. In table 10 the diagonal main constants are compared with those of  $\alpha$ -methylthiophene. The difference  $f_{\text{C}=\text{C}} - f_{\text{C}-\text{C}}$  between thiophene (or methylthiophene) and polythiophene, showing partial delocalisation of the double bond, should be noted. The binding constant  $f_{\text{C}_{\text{ex}}-\text{C}-\text{B}}$ , between the methyl radical and the thiophenyl ring in methylthiophene is approximately half the corresponding constant between two thiophenyl rings in polythiophene, indicating that the polymer is rather rigid.

The dispersion curves and the density of states for PT are reported in figure 3 (except for the modes near  $3000 \text{ cm}^{-1}$ ) and figure 4. We can see that in figure 3 the dispersion is very weak for modes with frequency higher than  $500 \text{ cm}^{-1}$ . These modes indeed present a molecular character.

These results explain the relative independence of the frequency with the length of the chain as observed by Furukawa *et al* (1987) and reproduced here in tables 1 and 2. However, the dispersion curves do not allow us to explain the frequency shift of the Raman mode near  $1500 \text{ cm}^{-1}$  observed for the first oligomers and this confirms the presence of a defect mode overlapping the normal lattice mode in PT.

**Table 9.** Internal force constants for PT.

Constant	Value (mdyn Å <sup>-1</sup> )	Constant	Value (mdyn Å rad <sup>-2</sup> )
Diagonal force constants in internal coordinates			
$f_{C=C}$	8.166(11)	$f_{\angle B_5-C-C_{ex}}$	2.256(8)
$f_{C-C}$	6.427(18)	$f_{\angle C-S-C}$	1.748(15)
$f_{C-H}$	5.130(3)	$f_{\angle C=C-C}$	1.192(4)
$f_{C-S}$	4.860(9)	$f_{\angle S-C=C}$	1.028(8)
$f_{C-C_{ex}}$	3.485(12)	$f_{\angle B_5-C-H}$	0.904(2)
Constant	Value (mdyn Å <sup>-1</sup> )	Constant	Value (mdyn rad <sup>-1</sup> )
Non-diagonal force constants in internal coordinates			
$f_{C=C, C=C}$	-0.435(11)	$f_{C^*=C, \angle B_5-C^*-C_{ex}}$	-0.414(6)
$f_{C=C, C^*-C}$	0.972(Sc)	$f_{C^*=C^*, \angle C^*=C^*-C}$	1.085(Sc)
$f_{C=C, C^*-H}$	-0.113(7)	$f_{C^*=C^*, \angle S-C^*=C^*}$	0.860(11)
$f_{C=C, C^*-S}$	0.204(14)	$f_{C=C^*, \angle B_5-C^*-H}$	-0.230(Sc)
$f_{C=C, C-C}$	-0.343(14)	$f_{C^*-C^*, \angle C=C^*-C^*}$	0.564(10)
$f_{C=C, C^*-C_{ex}}$	0.101(7)	$f_{C^*-C, \angle B_5-C^*-H}$	0.118(4)
$f_{C^*-C, C^*-H}$	$f_{C=C, C^*-H}$	$f_{C^*-S, \angle B_5-C^*-C_{ex}}$	0.491(8)
$f_{C-C, C-S}$	-1.265(9)	$f_{C^*-S^*, \angle C-S^*-C^*}$	0.983(15)
$f_{C-S^*, C-S^*}$	0.580(8)	$f_{C^*-S^*, \angle S^*-C^*=C}$	1.372(5)
$f_{C^*-S, C^*-C_{ex}}$	-0.642(6)	$f_{C^*-C^*_{ex}, \angle C^*_{ex}-C^*-B_5}$	0.304(5)
		$f_{C^*-C_{ex}, \angle C=C^*-S}$	-0.435(5)
Constant	Value (mdyn Å rad <sup>-2</sup> )	Constant	Value (mdyn Å rad <sup>-2</sup> )
Non-diagonal force constants in internal coordinates			
$f_{\angle C_{ex}-C^*-B_5, \angle C^*-C^*_{ex}-B_5}$	-0.245(8)	$f_{\angle C=C^*-C^*, \angle C^*-C^*=C}$	0.000(fix)
$f_{\angle B_5-C^*-C_{ex}, \angle C-S^*-C^*}$	0.246(8)	$f_{\angle C^*=C^*-C^*, \angle S-C^*=C^*}$	0.088(3)
$f_{\angle B_5-C^*-C_{ex}, \angle C^*=C-C}$	0.189(8)	$f_{\angle C=C-C^*, \angle H-C^*-B_5}$	0.000(fix)
$f_{\angle B_5-C-C_{ex}, \angle B_5-C-H}$	0.020(Sc)	$f_{\angle S-C=C^*, \angle B_5-C^*-H}$	0.040(Sc)
$f_{\angle C-S^*-C^*, \angle S^*-C^*=C}$	0.000(fix)	$f_{\angle B_5-C-H, \angle H-C^*-B_5}$	-0.080(2)

\* , \* , common atoms; B<sub>5</sub>, any external bisector; C<sub>ex</sub>, this carbon is in the next cycle. For each adjusted parameter the significance is given in the last digit. (Sc), value fixed to the thiophene value given by Scott (1969); (fix), cancelled parameter.

**Table 10.** Main force constants for  $\alpha$ -methylthiophene and PT.

Constant	Value (mdyn Å <sup>-1</sup> )		Constant	Value (mdyn Å rad <sup>-2</sup> )	
	Methylthiophene	PT		Methylthiophene	PT
$f_{C=C}$	8.704	8.166	$f_{\angle C_{ex}-C-B_5}$	1.224	2.256
$f_{C-C}$	6.574	6.427	$f_{\angle C-S-C}$	1.596	1.748
$f_{C-H}$	5.193	5.130	$f_{\angle C=C-C}$	1.173	1.192
$f_{C-S}$	4.794	4.860	$f_{\angle S-C=C}$	1.173	1.028
$f_{C-C_{ex}}$	4.406	3.485	$f_{\angle B_5-C-H}$	0.870	0.904

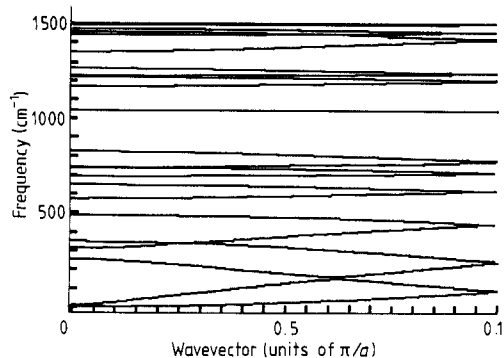


Figure 3. PT calculated dispersion curves.

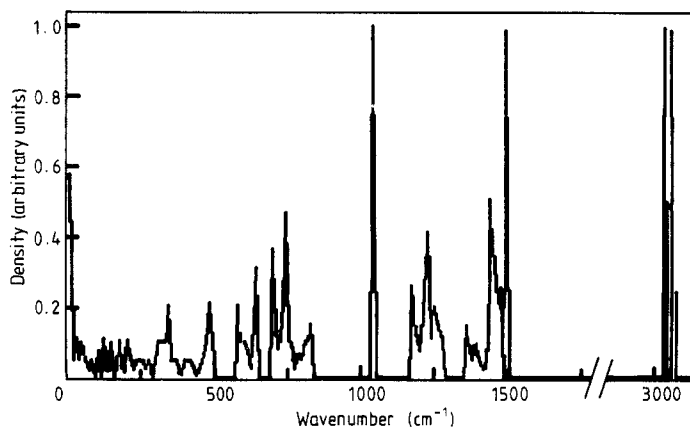


Figure 4. PT calculated density of states.

To check these results we have also calculated the infrared and Raman frequencies of active modes for finite PT chains with C–H bonds at the extremities and also the frequencies obtained with finite chains with cyclic boundary conditions. These frequencies are not in fact very sensitive to the length of the chain (2, 4, 6 or 8 rings) and are very close to those derived for the infinite chain.

### 5.2. First-order infrared activity

In order to determine the effects due to the vibronic enhancement in the infrared spectra, we have calculated the dielectric constant and the absorption coefficient of a neutral chain using a classical model where the atoms carry a weak charge. The dielectric constant is given by

$$\varepsilon(\omega) = \varepsilon(\infty) + \frac{4\pi}{V_a} \sum_j \frac{S_j^2}{\omega_j^2 - \omega^2 - i\gamma_j}$$

where  $\omega_j$ ,  $S_j$  and  $\gamma_j$ , respectively, are the frequency, the oscillator strength and the

**Table 11.** Infrared peak strengths for PT (experimental and theoretical); w, weak; m, medium; s, strong.

Wavenumber (cm <sup>-1</sup> )	Relative experimental strength	Relative calculated strength
580	m	s
695	m	s
739	w	w
825	m	m
1040	w	w
1225	m	w-m
1356	w-m	m
1439	m	w
1492	m-s	m
3063	s	m
3100	m	m

damping of the oscillator  $j$ ,  $V_a$  is the volume of the unit cell and

$$S_{aj} = \sum_n \frac{1}{\sqrt{m_n}} q_n e_{an} \left( \begin{matrix} \mathbf{k} = \mathbf{0} \\ j \end{matrix} \right)$$

where  $q_n$  and  $m_n$  are the charge and the mass of atom  $n$ ,  $e_{an} \left( \begin{matrix} \mathbf{k} \\ j \end{matrix} \right)$  is the  $an$  component of eigenvector of the mode  $(\mathbf{k}, j)$ . The  $q_n$  are taken as parameters ( $\sum_n q_n = 0$ ). We need only the relative intensity for the infrared peaks; so the unit of  $q_n$  is chosen arbitrarily. Only the ratios  $q_s/q_{c_\alpha}$  and  $q_{c_\beta}/q_{c_\alpha}$  are adjusted in order to fit approximately the observed infrared spectrum.

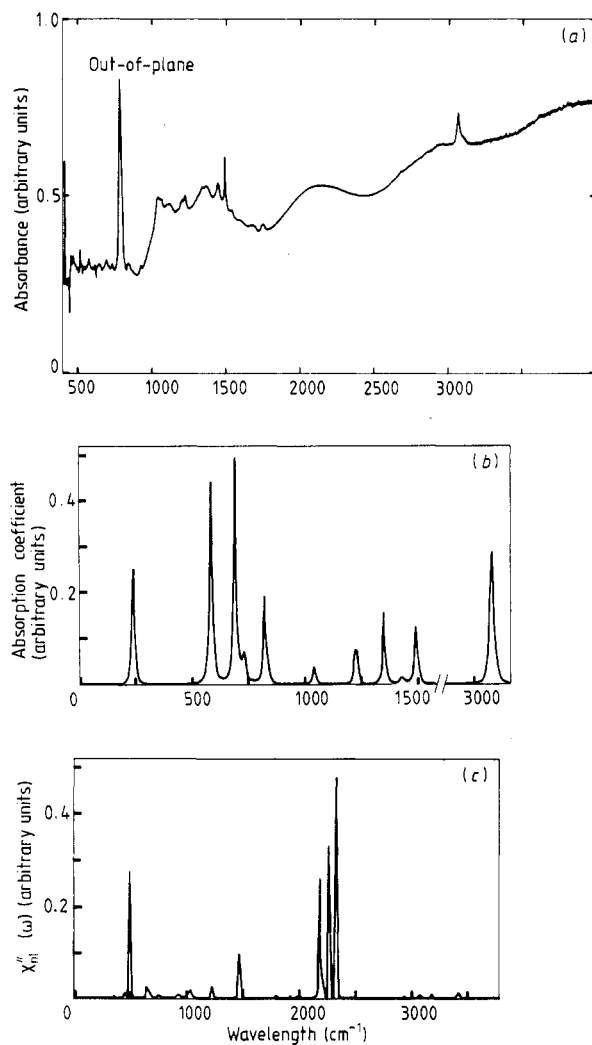
Figure 5(a) gives experimental infrared spectra recorded by Hasoon *et al* (1989). Figure 5(b) shows the calculated infrared transmission at first order. Qualitative comparison of the relative experimental and calculated strengths is shown in table 11. It should be noted that, for instance, the ratio of the calculated intensities of the 1439, 1492 or 3063 cm<sup>-1</sup> lines to the 580 cm<sup>-1</sup> line is weaker than the corresponding experimental value. These discrepancies show that, while the values of the frequencies of the peaks are very well determined by a classical force field model, their intensities cannot be explained by a simple atom charge model and it is necessary to include in the intensity calculation the contribution due to the phonon-electron coupling (vibronic enhancement).

### 5.3. Second-order infrared spectra

In order to discuss the nature of the supplementary bands, which are not explained by first-order absorption, we have also determined for the infinite chain the second-order infrared spectra. We follow the same method as developed in detail by Benoit and Giordano (1988) and by Giordano (1988). The second-order contribution to the imaginary part of the susceptibility is given by

$$\chi_{ni}(\omega) \sim \sum_{\mathbf{k}, ij} \left| M \begin{pmatrix} \mathbf{k} & -\mathbf{k} \\ i & j \end{pmatrix} \right|^2 g(\mathbf{k}, i, j, \omega)$$

where  $g(\mathbf{k}, i, j, \omega)$  is the two-phonon propagator.



**Figure 5.** (a) PT experimental infrared transmission (Hasoon *et al* 1989); (b) PT calculated infrared transmission (first order); (c) PT calculated infrared susceptibility (second order).

The coefficients  $M\left(\begin{smallmatrix} k & -k \\ i & j \end{smallmatrix}\right)$  are calculated for all modes  $i$  and  $j$  with wavevectors  $\mathbf{k}$  and  $-\mathbf{k}$  in the first Brillouin zone. They are deduced from the variations in the atom electric charges  $M_{\alpha m, \beta n}$  with atomic motions through the relation

$$M\left(\begin{smallmatrix} \mathbf{k} & -\mathbf{k} \\ i & j \end{smallmatrix}\right) = \sum_{\alpha m, \beta n} \frac{1}{\sqrt{m_m m_n}} M_{\alpha m, \beta n} e_{\alpha m}\left(\begin{smallmatrix} \mathbf{k} \\ i \end{smallmatrix}\right) e_{\beta n}\left(\begin{smallmatrix} -\mathbf{k} \\ j \end{smallmatrix}\right).$$

To obtain the  $M_{\alpha m, \beta n}$  coefficients, we suppose that each atomic electric charge  $q_m$  is a linear function of the lengths of all bonds which contain the atom  $m$ . When all symmetry properties are taken into account, there are only seven independent coefficients which are chosen arbitrarily.

Figure 5(c) shows the calculated second-order infrared spectrum obtained with these

$M_{\alpha m, \beta n}$  coefficients. Comparison with experimental results shows that the broad 2200–2300  $\text{cm}^{-1}$  peak could be explained by combinations of phonons of the first Brillouin zone. We find a medium peak at 500  $\text{cm}^{-1}$  which could also be the experimental peak observed at 520  $\text{cm}^{-1}$ .

#### 5.4. Discussion

The out-of-plane modes for PT not taken in account by our present model appear experimentally at low frequencies not very far from the corresponding thiophene modes. The experimental infrared peaks for PT at 452, 785 and (perhaps) 714  $\text{cm}^{-1}$  can be easily assigned to such modes, but the number of required parameters of the harmonic potential is too large to allow a suitable fitting.

So we can conclude that the remaining modes observed at 846, 1140, 1203 and 1341  $\text{cm}^{-1}$  probably arise from the presence of defects in the PT chain.

In this work we have presented a dynamical model for infinite and finite chains of PT. This model accounts very well for the frequencies of optical modes. The results show that it is not necessary to include the long-range forces for electron–phonon coupling. With this very nice model, we shall use these results to study, on the one hand, chains with topological defects and, on the other hand, chains with chemical defects, e.g. the bond between two thiophenyl rings in the  $\beta$  position. Such a study is possible by means of the spectral moment method.

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