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Far Infrared and Raman Spectroscopic Investigations of the Lattice Modes of Crystalline Thiophene

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Vibrational spectroscopic measurements combined with the lattice statics and lattice modes calculations have been applied in order to derive the most probable structure of the low temperature (stable) phase V of thiophene (below 112 K). The far infrared spectrum has been recorded from 135 to 30 cm^{-1} of this phase of thiophene at 20 K. The low frequency Raman spectrum from 150 to 10 cm^{-1} has also been recorded for the phase V at 35 K. From the fact that there is coincidence between lattice mode frequencies observed in the infrared and Raman spectra, one can exclude centrosymmetric space groups. The observations of 20 lattice modes in the Raman spectrum and 14 modes in the FIR spectrum eliminate the possibility of tetragonal symmetry, but the data are consistent with orthorhombic symmetry with the unit cell containing 4 molecules on C_1 sites. In spite of the glassy-like transition observed for this phase at 42 K, both spectra bear striking resemblance to the typical low frequency spectra of molecular crystals. Therefore, it is assumed, for the purposes of the static and dynamic studies, that the thiophene in phase V can be considered as an ideally ordered crystal. Calculations of the lattice energy and lattice mode frequencies, based on the atom-atom potential, appear to be most consistent with space group $Pca2_1$ (C_{2v}^5) which is in agreement with most of the earlier predictions made for the structure of the thiophene phase V.

The Raman spectrum of the metastable phase II$_2$ is also given.

INTRODUCTION

The first information on different crystalline modifications in solid thiophene, C_4H_4S, was provided by Waddington *et al.*[1] who reported results on the thermodynamic properties of this compound and, from the measurements of the heat capacity, discovered the existence of the four crystalline phases.

Investigations of the structures of different phases have been performed by x-ray diffraction[2,3] IR absorption[4,5,6] Raman scattering[7], NMR spectroscopy[8,9] measurements with modest success. Waddington could establish that the first phase (235—171 K) is plastic with four molecules in the unit cell. From the early x-ray data[2] it was not possible to distinguish between the space groups *Aba* 2 (C_{2v}^{17}) or *Cmac* (D_{2h}^{18}). For the other phases there were only fragmentary indications about the crystal symmetry and the number of molecules in unit cells. Several authors have reported that the ordered phase, below 112 K, has the unit cell with four molecules in C_1 position. However, these investigators do not agree whether the structure of this phase is tetragonal[3,4] or orthorhombic.[2,5,6,7] The uncertainty about the number of the phase transitions in thiophene became more pronounced when Migliorini *et al.*[7] observed an entirely different Raman spectrum on a sample prepared by rapid cooling from the high temperature phase to very low temperatures. In this situation, a systematic investigation of the different phases of thiophene has been undertaken in the last few years by the group at the Université Paris-Sud. They performed detailed calorimetric[10–13] and x-ray diffraction[14,15] studies. The most important result obtained is the recognition of the existence of the two phase sequences: one stable and one metastable solid phase.[10,11] Accordingly, they gave also a new classification of the observed phases which is also used in the present paper (Figure 1). This result explained the earlier confusing observations in NMR[8] and Raman spectroscopic[7] measurements. X-ray measurements confirmed the earlier proposed space group *Cmca* for phase I and determined the group *Pnma* for phase III. In particular, the molecular packings in both phases are of herringbone structure with in-plane orientational disorder.[14] Further x-ray investigations indicated that phases II', II$_1$ and II$_2$ correspond to superstructures of the orthorhombic lattice of phase I with which they are not commensurate.[15] Recent calorimetric studies have shown that around 40 K each phase sequence exhibits a glassy transition.[13] This phenomenon has been attributed to the freezing of the reorientational molecular motion in the ordering process. Finally, the low frequency Raman spectra were recorded for all phases in both sequences.[14]

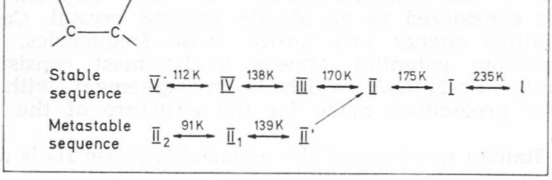


Figure 1. Shematic representation of the two sequences of phase transitions in thiophene. Notation used is according to Ref. 11. In the insert is the definition of the molecular inertial system.

Direct x-ray measurements of the phases in the stable sequence were not performed, probably because these crystals usually shatter when they are cooled through the phase transition to the ordered phase. Observing the behaviour of the NMR line width at the III—IV and IV—V transitions, the authors anticipate that the molecular packing in phase V could be of herringbone pattern,[15] but do not discuss the structure nor the number of molecules in the lattice of this phase.

Consequently, it can be assumed that this number is still four molecules as it was found in earlier infrared[4,7] and x-ray[3] measurements.

The aim of the present study is to obtain the frequencies for the lattice modes of phase V by both far infrared and Raman spectroscopy. These data should confirm the assumption of four molecules in the unit cell in a more direct way than by observing the splitting of internal modes.[4,5,6] It is also expected that these data could be used to determine whether phase V is orthorhombic[2,7] or tetragonal.[3,4]

As the authors themselves asserted, the impact of the observed glassy-like transition on Raman and infrared spectra is not significant[16] and will be discussed latter on in connection with the static and dynamic calculations performed for the lattice of phase V of thiophene.

EXPERIMENTAL

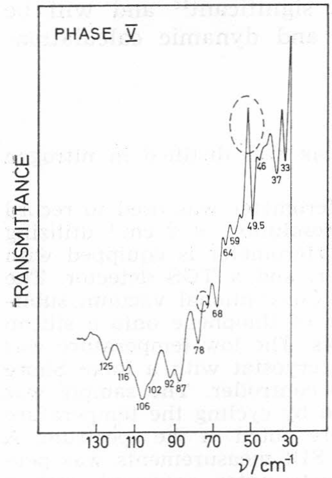
In all measurements thiophene from Eastman-Kodak was distilled in nitrogen atmosphere before each measurement.

A Digilab model FTS-15B Fourier transform interferometer was used to record the far infrared spectrum (135 to 30 cm^{-1}) at typical resolution of 2 cm^{-1} utilizing 500 scans for the reference and sample data. This interferometer is equipped with a high pressure Hg arc source, 12.5 Mylar beamsplitter, and a TGS detector. The interferometer housing was purged with dry nitrogen. Conventional vacuum sublimation tehnique were employed to deposit a solid film of thiophene onto a silicon plate held in a cell equipped with polyethylene windows. The low temperature was maintained by a Cryogenics Technology Inc. Spectrum cryostat with a Lake Shore Cryotronic model DTL-500 high precision temperature controller. The sample was initially deposited at 30 K and then repeatedly annealed by cycling the temperature between 30 K and 110 K until no further changes were noted in the spectrum. A typical spectrum is shown in Figure 2. Another set of FIR measurements was performed using a Grubb Parson Fourier transform spectrometer equipped with a Si +TPX beamsplitter. In this case the sample was placed between polyethylene windows and then slowly cooled. Excellent coincidence exists between the frequencies observed in both series of measurements as it can be seen in Figure 3 where the temperature dependence of the observed FIR and Raman frequencies is given.

Raman spectra of polycrystalline samples at temperatures including solid phases in the range 223—35 K (Figures 4 and 5) were recorded with a Coderg model T800 spectrometer utilizing an Ar ion laser operating on the 5145 Å line. The Raman cell containing cca 1 cm^3 of sample, was placed in a cryostat where it was cooled by a controlled stream of helium gas. The cooling procedure was always very slow to prevent formation of the metastable phase, and in addition the sample was kept at least 15 minutes at the chosen temperature before starting the recording of the spectrum. On the contrary, the spectrum of phase II$_2$ (Figure 6) was obtained by quick cooling of the sample from phase I to the low temperatures. The difference between this spectrum and those of the stable phase V (Figure 5) is evident. The similarity of the present Raman spectra with those reported by André *et al.*[11] should also be stressed.

RESULTS AND DISCUSSION

Figure 4 shows the Raman spectra of stable phases sequence of solid thiophene in the temperature range 223 to 150 K. The notation of the phases is according to the one proposed by André *et al.* (Figure 1). The broad bands in the Raman spectra of phases I, II' and III are typical of those for disordered crystals in complete accordance with the structural findings reported for these phases.[2,14] The big change in the Raman spectrum at transition II—III corresponds to similar phenomena observed in heat capacity and enthalpy measurements and are obviously connected with the change in the crystal structure observed by x-ray measurements.[14]



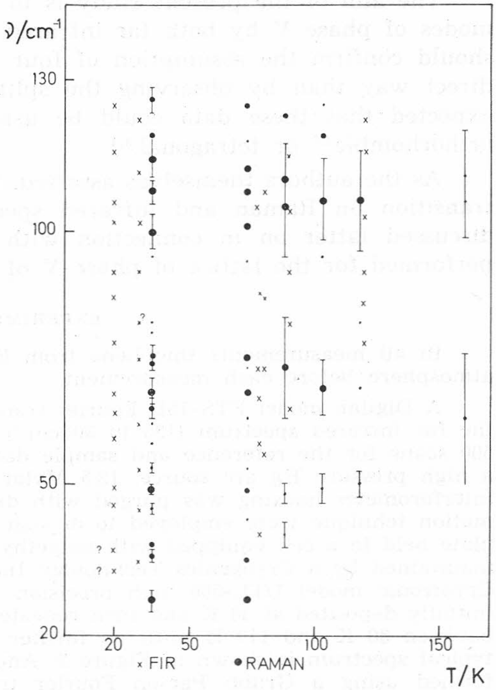


Figure 2. Far infrared spectrum of polycrystalline thiophene at 20 K in phase V. The dashed ellipse at ≈50 cm⁻¹ indicates an instrumental artifact and the one at 72 cm⁻¹ is due to the polyethylene windows.

Figure 3. Temperature dependence of the lattice vibrations of thiophene. The vertical bars indicate, approximately, the width of the Raman bands and the radii of the circles indicate their approximate intensities.

Figure 5 shows the Raman spectra of phase V at different temperatures. While at a temperature near the phase transition the broad spectral features still persist, with decreasing temperatures these bands at 35 K split in a number of sharp lines.

Although the infrared spectroscopy has been often used in the investigation of thiophene, as far as we know, the FIR spectrum shown in Figure 2 is the first attempt to use this method in order to complete the lattice vibrational spectrum of phase V. All earlier similar investigations were performed in the middle infrared spectral range.[4,5,6]

In all spectra recorded at lowest temperatures 19 or 20 Raman bands were observed, which is in accordance with the prediction of four molecules in the unit cell.[3,4,7] From similar measurements André *et al.*[11] reported 22 Raman lines at 12 K. Apart from the fact that this result should be confirmed

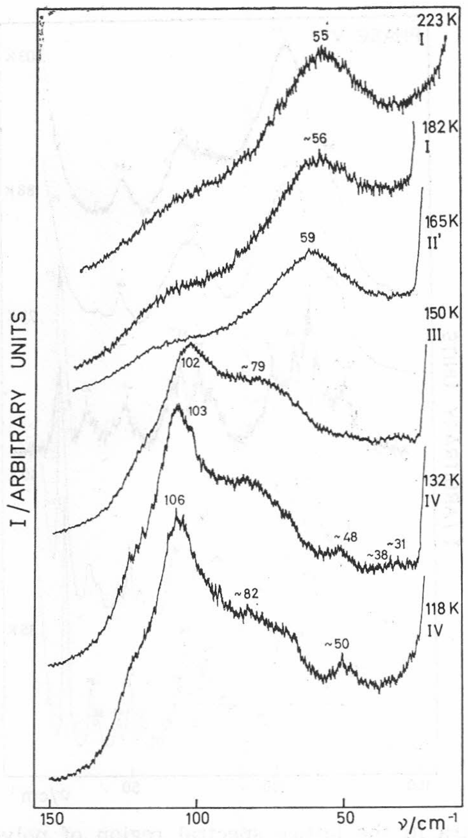


Figure 4. Raman spectra in the lattice spectral region of polycrystalline thiophene in the first four stable phases.

by some other measurements,[17] it is difficult to admit that the appearance of only one band in excess is a proof of a larger number of molecules in the unit cell.

The lattice mode frequencies observed in the Raman spectrum at 35 K agree very well with the frequencies obtained in the far infrared spectrum at 20 K (Figure 2), which is a proof that the space group for phase V is not centrosymmetric, in contrast to the conclusion of Paliani *et al.*[6].

Starting with the assumption that the unit cell of phase V contains four molecules on C_1 position, we considered the tetragonal and orthorhombic space groups which permit these conditions. From the corresponding factor groups we have calculated the number of expected infrared and Raman lattice modes ($Z = 4$, site C_1) for each of these groups and these results are given in Table I. As it can be seen from this table, the number of observed infrared and Raman lattice modes is consistent with the orthorhombic space groups but not with the tetragonal ones. This conclusion fits well in the frame of investigations of the structure of phase III which is orthorhombic[7], since as already mentioned, the Raman spectrum for phases III, IV and V do not indicate important chan-

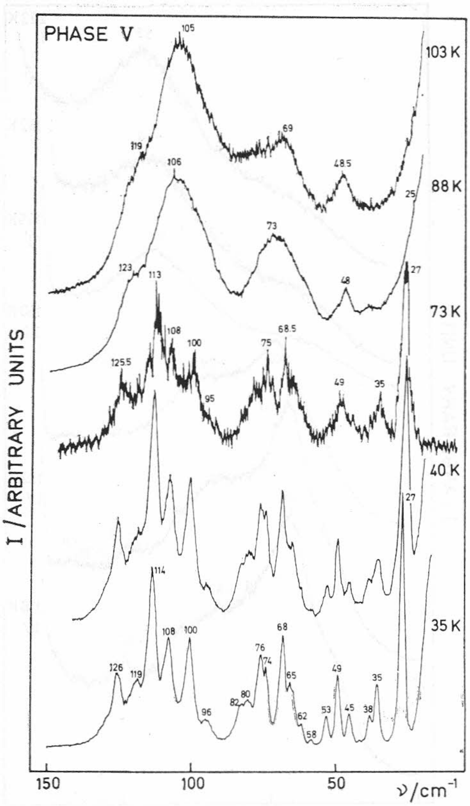


Figure 5. Raman spectra in the lattice spectral region of polycrystalline thiophene at different temperatures in stable phase V.

ges and it has been concluded that these phases are probably orthorhombic too.[14]

TABLE I

The Number of Expected[a] and Observed Raman and Infrared Frequencies for Phase V of Crystalline Thiophene

Space group symmetry	Factor group	Number of expected Raman frequencies	Number of expected infrared frequencies	Number of observed Raman frequencies	Number of observed infrared frequencies
Tetragonal	C_4	15	12	20	14
	S_4	15	8		
Orthorhombic	C_{2v}	21	15		
	D_2	21	15		

[a] Based on the assumption that the unit cell contains four molecules on C_1 sites.

All conclusions quoted so far have been drawn from spectroscopic data obtained in the present measurements. Without pretending to have given final determination of the crystal structure of thiophene V, we believe that the vibrational spectroscopy combined with the calculations of the static properties (lattice energy, lattice parameters and molecular positions and orientations), as well as the normal mode calculations, could determine the most probable space group between the four proposed from the orthorhombic crystal system, thus contributing to a better understanding of thiophene V.

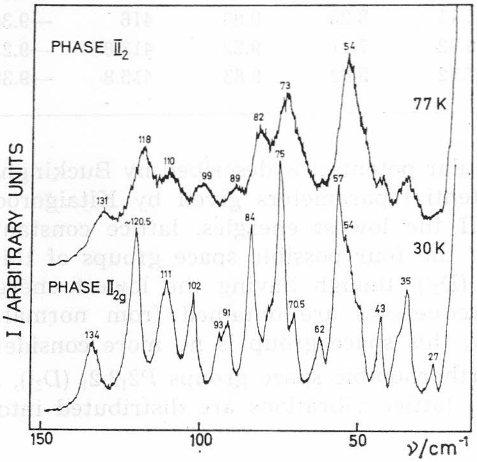


Figure 6. Raman spectra in the lattice spectral region of thiophene metastable phase II_2 obtained by quick cooling from phase I.

At this point it is necessary to discuss the phenomenon of the glassy transitions observed in the low temperature phases. The remark that, as a consequence of the structural disorder, the Raman bands are broad[11] is true for the spectrum of the metastable phase II_2, as shown in Figure 6. It is difficult to say the same about the bands of the stable phase V (Figure 5), since their band-widths are comparable with those in the lattice spectrum of the ordered phase of furan, C_4H_4O, crystallizing also with four molecules in the unit cell[18]. Measurements of the FWHM of the band 27 cm^{-1} at 40, 35 and 20 K give values 6.5, 4 and 2 cm^{-1}, respectively, showing a further narrowing of the bandwidths at decreasing temperature even after formation of the glassy state. In addition, the experimental data[13] indicate that phase V is much less disordered than phase II_2. Similarly, slightly disordered molecular solids do not perturb strongly the long phonon waves, which is in full accordance with earlier observations[16].

All these facts indicate that phase V can be, in the first approximation, considered an almost ordered structure. In these conditions, the lattice vibrational analysis and calculations of lattice static properties can be performed.

Calculations of lattice energy were performed minimizing the total energy with respect to all independent variables in an orthorhombic unit cell containing four molecules using the Fletcher[19] quasi-Newton minimization method. There are nine variable parameters, three lattice constants *a*, *b*, *c* position and orientation of the molecule within the unit cell.

TABLE II

Calculated Lattice Constants and Energies for Four Possible Space Group of Thiophene V

Space group	a/Å	b/Å	c/Å	V/Å^3	$U_0/\frac{\text{kcal}}{\text{mol}}$	Stability of the crystal lattice
$P222$ (D_2^1)	6.12	6.46	10.64	421	—9.55	Unstable
$P2_12_12_1$ (D_2^4)	5.11	8.25	9.83	416	—9.38	Stable
$Pca2_1$ (C^5_{2v})	6.02	7.11	9.82	413.8	—9.25	Stable
$Pna2_1$ (C^9_{2v})	7.52	5.62	9.83	415.8	—9.38	Stable

The intermolecular potential is described by Buckingham 6-exp atom-atom potential using potential parameters given by Kitaigorodskii[20] and Naučitelj *et al.*[21]. In Table II the lowest energies, lattice constants, unit cell volume and the stability of the four possible space groups of thiophene V are given. Space group $P222$ (D_2^1), though having the lowest energy, is unstable since some imaginary frequencies are obtained from normal coordinate calculations. Consequently, this space group is no more considered.

Utilizing the orthorhombic space groups $P2_12_12_1$ (D_2^1), $Pna2_1$ (C^9_{2v}), or $Pca2_1$ (C^5_{2v}) the 21 optical lattice vibrations are distributed into four classes as follows:

$$D_2 \ \Gamma\,(OT \ and \ OL) = 6A + 5B_1 + 5B_2 + 5B_3$$

$$C_{2v} \ \Gamma\,(OT \ and \ OL) = 5A_1 + 6A_2 + 5B_1 + 5B_2$$

All of these species are active in the Raman spectrum whereas all but the A or A_2 modes are infrared active.

The normal coordinate calculation was performed in the rigid-body approximation using the method as given by Pawley[22]. The great difference between the lowest internal (452 cm^{-1})[4,7] and the highest external (126 cm^{-1}) vibrational frequencies justifies the use of the rigid-body approximation.

In Table III, the results of normal coordinate calculations are listed for all space groups considered. In assigning the observed bands to the calculated frequencies we started from the bands which are infrared inactive, *i. e.* A or A_2, depending on the space group. The assignment of the remaining bands follows the distribution of the calculated frequencies. The best agreement is obtained for space group $Pca2_1$ (C^5_{2v}).

In Table IV, assignment of the observed bands is proposed according to the molecular motion defined by the eigenvectors obtained for space group $Pca2_1$ (C^5_{2v}), indicating the smallest differences between the observed and calculated frequencies. Rotational and translational movements are related to the inertial axes (U, V, W) of the molecule as defined in Figure 1.

The molecular positions and orientations in the unit cell, as derived from lattice energy calculations, are not far from the herringbone pattern, which indicates that the structure obtained for the thiophene phase V is among those predicted by Figuière *et al.*[11] on the basis of the NMR data.

TABLE III

Lattice Energy and Normal Coordinate Calculations for the Possible Space Groups of Thiophene V

Space group				$P2_12_12_1$			$Pna2_1$			$Pca2_1$	
Calculated lattice energy (kcal/mol)				—9.38			—9.377			—9.25	
Unit cell volume (Å^3)				416			415.8			413.8	
	Raman	FIR									
	ν_{obs}			ν_{calc}	ν_{calc}—ν_{obs}		ν_{calc}	ν_{calc}—ν_{obs}		ν_{calc}	ν_{calc}—ν_{obs}
FIR inactive	119		A	141.6	+22.6	A_2	143	+24	A_2	136.5	+17.5
	80			119	+39		123.5	+43.5		123.6	+43.6
	74			66.2	—7.8		95.7	+21.7		88.3	+14.3
	62			61.1	—0.8		61.7	—0.3		87.9	+25.9
	53			46.5	—6.5		50.5	—2.5		54	+1
	27			35	+8		34.6	+7.6		33.8	+6.8
FIR and Raman active	—	—	B_2	142.4		B_1	143.2		B_1	142.1	
	126	125	B_1	142.0	+16	B_2	142.1	+16.1	B_2	133.3	+7.3
	114	116	B_3	123.3	+9.3	B_2	122.7	+8.7	B_2	121.0	+7
	108	106	B_1	122.3	+14.3	A_1	120	+12	B_2	104.4	—3.6
	100	102	B_2	114.8	+14.8	B_1	116.5	+16.5	A_1	98.5	—1.5
	96	92	B_1	102.6	+6.6	B_1	101.3	+6.3	B_1	97.8	+2.8
	82	87	B_3	95	+8	B_2	89.6	+2.6	B_1	90.7	+3.7
	76	78	B_1	90	+13	B_1	71	—5	A_1	77.6	+1.6
	68	68	B_2	72	+4	A_1	66.2	—1.8	A_1	72.2	+4.2
	65	64	B_3	64.6	+0.6	A_1	63.6	—1.4	B_1	68.2	+3.2
	58	59	B_1	62.1	+4.1	B_1	62	+4	B_2	61.7	+3.7
	49	49	B_2	59	+10	B_2	59	+10	A_1	55.3	+6.3
	45	46	B_3	57.4	+12.4	A_1	56	+12	B_2	52.1	+7.1
	38	37	B_3	51.3	+13.3	A_1	46.3	+8.3	B_1	28.8	—9.1
	35	33	B_2	31	+4	B_2	30.8	—4.2	A_1	21.3	—13.7

It should be emphasized that from the present calculations of lattice mode frequencies, it comes out that all frequencies of the in-plane librational modes (around U axis) lie in the range 60—85 cm^{-1}. This is in fact the spectral range where the most important changes in the spectrum occur at phase transitions II—III and IV—V. This confirms the previous assumption that the in-plane rotational molecular motion of thiophene plays an important role in the dynamics of its crystal.

CONCLUSIONS

The results obtained do not surpass the frame of all the so far proposed structures for the crystal of thiophene V. The results could be separated into two groups:

From the spectroscopic data the following conclusions on the structure of the phase V can be drawn:

— Because of the coincidence between the Raman and FIR frequencies the centrosymmetric system is excluded.

— From the number of the observed Raman and FIR frequencies, assuming

TABLE IV

Proposed Assignment of the Phonon Spectrum for the Pca2$_1$ *Lattice of Thiophene V*

Symmetry	Calculated ν (cm^{-1})	% Rotation	Eigenvector	Observed (cm^{-1})	
				Raman	FIR
A_1	98.5	79	$R_v+T_u+T_w$*	100	102
	77.6	99	R_u+R_w	76	78
	72.2	2	$T_u+T_w+R_v$	68	68
	55.3	17	$T_w+T_u+R_v$	49	49
	21.3	99	R_w+R_u	35	33
B_1	142.1	99	R_w	—	—
	97.8	93	R_v+T_w	95	92
	90.7	43	T_v+R_u	82	87
	68.2	56	$R_u+T_v+R_w$	65	64
	28.8	6	$T_w+T_u+R_v$	38	37
A_2	136.5	96	R_w	119	
	123.6	54	R_v+T_u	80	
	88.3	40	$T_u+R_v+T_w$	74	
	87.9	94	R_u+T_v	62	
	54.0	4	$T_w+T_u+R_v$	53	
	33.8	8	$T_v+R_w+R_u$	27	
B_2	133.3	88	R_w+T_v	126	125
	121.0	60	$R_v+T_u+T_w$	114	116
	104.4	39	$T_u+R_v+T_w$	108	106
	61.7	67	$R_u+T_v+R_w$	58	59
	52.1	43	T_v+R_u	45	46

* Rotational and tranlational movements are related to the inertial axes (u, v, w) of the molecule, as defined in Figure 1.

that the unit cell contains four molecules, the tetragonal symmetry is eliminated.

From the lattice energy and normal mode calculations it follows:

— The most probable space group is *Pca*2$_1$

— The molecular packing is close to the herringbone-pattern

— The most temperature sensitive vibrational frequencies are connected with the in-plane rotational movement of the molecule.

We believe that these results have reduced the number of ambiguities about the structure of phase V and that they will be helpful to the crystallographic studies which could be undertaken in the future.

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SAŽETAK

Daleka infracrvena i ramanska istraživanja vibracija rešetke kristala tiofena

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Vibracijska spektroskopska mjerenja kombinirana su s modelskim računima strukture i vibracijskog spektra kristalne rešetke u svrhu određivanja najvjerojatnije strukture niskotemperaturne (stabilne) faze V tiofena (ispod 112 K). Apsorpcijski spektar u dalekom infracrvenom području snimljen je na temperaturi od 20 K u području od 135 do 30 cm^{-1}. Niskofrekventni Raman spektar (150—10 cm^{-1}) snimljen je za tu istu fazu na temperaturi od 35 K. Koincidencija frekvencija opaženih u infracrvenom i Raman spektru isključuje mogućnost centrosimetrične grupe za ovu rešetku. S druge strane postojanje 20 Ramanovih i 14 infracrvenih vrpci rešetke eliminira mogućnost tetragonalne simetrije ali je u skladu sa ortorombskom simetrijom uz jediničnu ćeliju koja sadrži četiri molekule u lokalnoj simetriji C_1. Usprkos staklastom stanju opaženom na 42 K oba ova spektra su vrlo slična tipičnim spektrima uređenih molekularnih kristala .Zbog toga se pri računu statičkih i dinamičkih svojstava kristala tiofen u fazi V može smatrati idealno uređenom tvorevinom. Račun energije rešetke i frekvencija modova rešetke, na osnovi atom-atom potencijala, pokazuju najbolje slaganje s prostornom grupom $Pca2_1$ (C^5_{2v}) što je u skladu sa nizom ranijih predviđanja za strukturu tiofena u fazi V. Dan je također Raman spektar metastabilne faze II_2.