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Electrochemical Synthesis and Vibrational Mode Analysis of poly (3-methelthiophene)

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Poly (3-methyl thiophene) thin films have been synthesized electrochemically on flat gold electrodes by anodic oxidation of monomer. The resulting polymers were characterized by cyclic voltammetry, FT-IR, and SEM techniques. Interpretation of experimental data was supported by the semi-empirical PM3, and ab initio calculations of the B3LYP/6-31G** using Hyperchem package. The computed vibrational spectra are in good agreement with the experimentally determined spectra.

Keywords: conducting polymers; poly (3-methylthiophene); electrochemistry; Infrared Spectroscopy; Scanning electron microscopy

1. INTRODUCTION

Polythiophene (PT), poly (3-methylthiophene) (P3MTh), polypyrrole (PPY), and polyaniline (PANi) are the most frequently used of the conducting polymers (CPs) in applications because of their interesting chemical and physical properties, such as batteries [1] super capacitors [2], sensors [3], field effect transistors [4], optical waveguides [5], optoelectronic devices [6], photovoltaic and photoconductive devices and optical modulators [7]. Polythiophenes have also been exploited in sensor applications [8-13], biosensors [14–15], corrosion protection [16] and microwave shielding [17]. P3MTh, which belongs to PT family, has good chemical and environmental stability. A characteristic feature is that the conductivity of these polymers can be widely varied ranging from the conducting to the insulating by doping. PT are promising materials among various classes of conducting polymers, because of their good thermal and chemical stability, as well as their optical and electronics properties, useful for various device applications such as LED [18], photovoltaic, photoconductive devices, and optical modulators [7]. These conducting polymers can be synthesized either chemically or electrochemically [19] mostly, by polymerization reaction with radicals as reactive agents [20]. With the exception of polyacetylene, all-important conducting polymers can be produced electrochemically by anodic oxidation. In this method, the polymer films are formed directly on the electrode surface, being in its doped (conducting) state. In comparison to standard chemical procedures, this method is advantageous, due to easy control of the growth process. Electrochemical synthesis of CPs (polypyrrole, polythiophene and poly (3-methylthiophene)) and their derivatives has attracted special attention as an easy and highly controllable preparation method for this important class of stable and dopable conducting polymers. The electrochemical polymerization is carried out by applying a positive potential between the working electrode and the counter electrode, with the current measured simultaneously, these electrodes are separated by an ionic solution. The primary role of the ions in the solution as a background electrolyte is to carry the current in the bulk solution between these electrodes. Consequently, there is a very high electric field at the surface of the electrodes depending on the applied voltage. This high field leads to electron transfer processes between the electrode and the molecules in the solution near the electrode surface, the electrochemical current can act as an oxidizing or a reducing agent. Electrodeposition of P3MTh was first achieved by Tourillon and Garnier, it showed an electrical conductivity range between 10 and 10^{-2} S/cm [19]. The electrical conduction mechanism of P3MTh is mainly due to electron hoping along and across the polymer chains with conjugated bonds [21, 22]. In this work, thin films of poly (3-methelthiophen) have been prepared by electro polymerization of 3-methylthiophene. Characterization of the resulting polymer was achieved using Fourier transform infrared spectroscopy (FTIR). Theoretical Vibrational modes frequencies are calculated and were compared with the experimental results. The present work is organized as follows: first, we give the experimental details and the calculation methods, then we report the infrared spectrum and discuss the assignments, and finally we present the results of the normal mode analysis in terms of theoretical frequencies.

2. EXPERIMENTAL PART

2.1. Materials

Acetonitrile, lithium tetrafluoroborate, and (3-methylthiophene) were provided from Aldrich and used without further purification. For preparation of the electrodes, they were cleaned by dipping in a 1:1 nitric acid solution for 10 s, then thoroughly washed with distilled water, and then displayed to torch flame. After that, they were polished with alumina slurry and washed with distillated water then the electrodes were dried in an oven for 1h at 170 ºC.

2.2. Electrochemistry

The electro-polymerization of (P3MTh) was performed in a one-compartment cell, using gold sheets as working counter electrodes (3x2 cm^2). Measurements were carried at room temperature; nitrogen bubbles deoxygenated the solution prior to electrochemical synthesis for 10 min before the experiment. The electrolyte is composed of Acetonitrile (solvent) and Lithium tetrafluoroborate (0.

1M). The concentration of 3-methylthiophene monomer was 0. 1 M. The polymer was deposited by applying +5V between the WE and CE for 10 min. Subsequently, the film was reduced by immersion in methanol. The thickness of our films was about 0.8 µm, some difficulties were encountered in scratching off the films from the Au electrode. The polymerization procedure is shown in Figure1; the first step is the formation of a positively charged species, which is a radical cation of the monomer. Then this radical cation reacts with another monomeric radical cation to form a dimmer. In the second step, the dimmer loses one electron to form a radical cation of the dimer, which either reacts with a monomeric radical cation to form a trimer, or reacts, with another dimeric radical cation to form a tetramer [23, 24]. The polymer chain models can be representing in various linkage modes (α-α′ substituted and α-β substituted) as shown in Figure1.

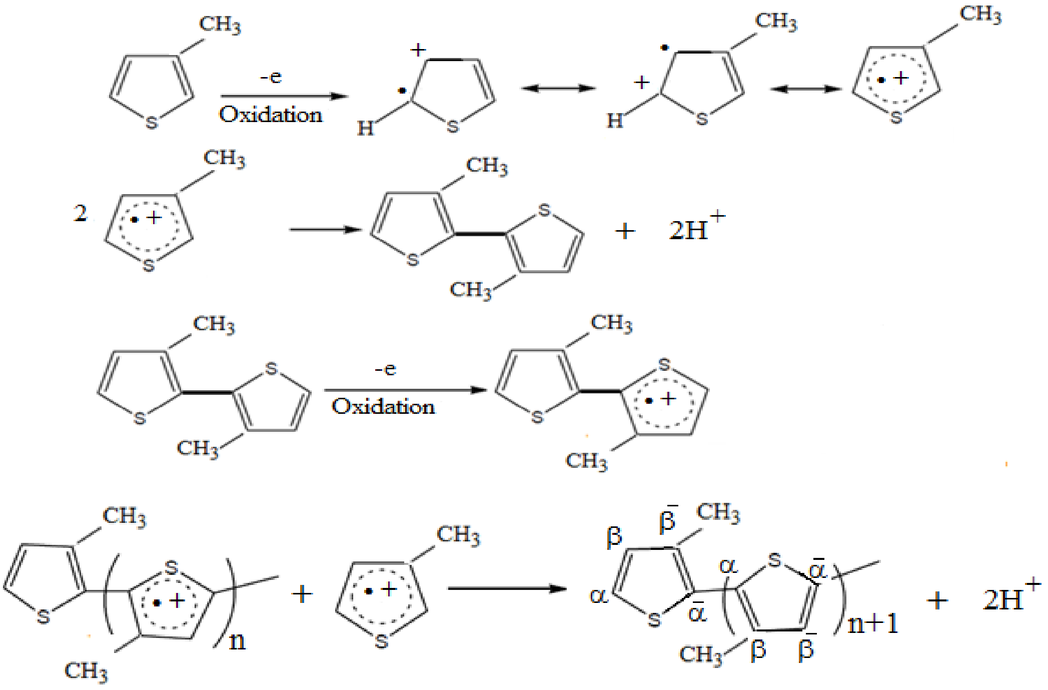

Figure 1. The Electro polymerization of (3-methelthiophene) Molecule

3. THEORETICAL PART

The molecule of (3-MTPh) is composed of 12 atoms, so it has 30 normal vibrational modes. We have taken into account two different symmetries depending on the configuration of the methyl group. If one of the methyl hydrogen atoms is coplanar to the aromatic ring, the proposed structure of poly (3-methylthiophene) will be as depicted in Figure.2 .The molecule has Cs group symmetry. On the basis of a Cs symmetry, the 30 fundamental vibrations of (3-MTPh) can be distributed as 20 A′+ 10 A″ and all these fundamentals frequencies are active in both IR and Raman spectra. Similarly, thiophene molecule has 21 fundamental C_{2v} symmetrical vibrational modes distributed in the four symmetry species and can be expressed as 8A1+7B2+3A2+3B1; here we have 14 modes of vibrations, which are active in both I.R and Raman (8A1+3A2+7B2) and (3B1) modes that are Raman active.

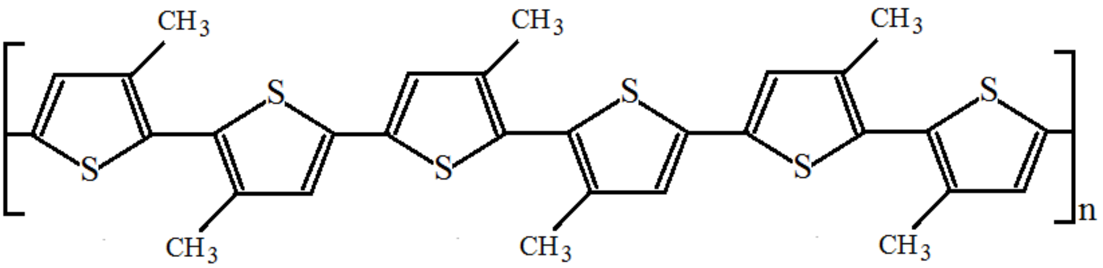

Figure 2. Possible Structure of Poly (3-methelthiophene)

4. RESULTS AND DISCUSSION

4.1. Morphology

The morphology of the P3MTh surface was examined by scanning electron microscope as seen in Figure 3. It is noted from the micrograph that there are some areas that indicates the presence of fiber-like structures. These fibres are constructed from some clusters few μm in diameter and small globular structures. The surface of the films is not smooth and there are pores of seemingly large size in the bulk of the films.

4.2. I.R Spectroscopy

Infrared spectra were recorded at room temperature using FTIR shimadzu spectrophotometer. I.R spectrum of (reduced) P3MTh thin films is shown in Figure 4. The assignments of the principal absorption bands are: the bands at 756 and 864 cm^{-1} are characterized by C-H out-of-plane bending and deformation vibrations respectively. The peak around 3400 cm^{-1} is absent in the spectrum of this polymer, indicating negligible humidity absorbance, i.e. no stretching vibrations of –OH of the carboxyl group exist [26, 27]. The week bands observed within 3000- 3100 cm^{-1} can be assigned to the aromatic C-H stretching vibrations [28, 29]. The low intensity bands appeared at 2860, and 2909 cm^{-1} are attributed to the deformation vibrations of the methyl group, asymmetric and symmetric stretching, respectively. The experimental infrared spectrum bands at 1438 and 1640 cm^{-1} are due to C=C stretching vibrations and the band at 1197 cm^{-1} and 1090 cm^{-1} are produced by C-H wagging vibrations [30,31] and, the band at 1165 is assigned to an in-plane C-H deformation. The peaks at 941, 925, 875, 783, 690 and 640 cm^{-1} correspond to C-S bonds in the polymer chains. [30, 32-35], whereas the peak at 609 cm^{-1} assigned to C-S-C ring deformation [36]. Infrared absorption around 567 cm^{-1}, which is assigned to plane vibrations of the ring. In addition, the two bands at 1379 and 1448 cm^{-1} can be assigned to twisting and rocking modes of the methyl groups or due to methyl deformation and ring stretching vibrations Cα=Cβ respectively [37]. The peak at 1446cm^{-1} is related to $C_{\alpha}=C_{\beta}$ stretching vibration of the thiophene ring [38]. The large signal at 1643 cm^{-1} can also be considered as a Cα=Cβ bond starching vibrations in the PT rings. [37, 39, 40] While, the band at 730 cm^{-1}, is attributed to C_{α}–C_{β} stretching mode [41]. The oxidized form of P3MTh shows a complex spectral pattern in the infrared spectrum, the intensities of some frequencies being overwhelmingly stronger than those of the pristine (reduced) material. This can clearly be seen in Figure 5. It can be also seen from this figure that there is a considerable change in the spectrum as compared with the well-known situation for intrinsic conducting polymers, this reflects the existence of charges on the polymeric chain, and the presence of these charges greatly increases the optical vibrational activity. Hence, the frequency changes of various vibrational modes in the infrared spectral region of the dopant molecule and it will be a strong modification spectrum between 1000 and 1500 cm^{-1} and a few rays significantly lower in the range 600 to 900 cm^{-1}. The infrared spectrum of liquid states of (3-methylthiophene) at room temperature have been recoded and measured, as shown in Figure 6. A general assignment of its vibrational fundamentals has been proposed and listed in Table 1. Finally, the bands of polythiophene have been also assigned.

4.3 Computational methods

Ab initio quantum chemistry calculations were conducted in this research for the 3-methelthiophen and thiophene coupled molecules at B3LYP/6-31G** level. We also used a Parameterized Model number 3 (PM3) semi-empirical method for calculating the vibrational modes, which is much faster than ab initio calculation methods. However, the results may or may not as accurate as those obtained using slower ab initio calculations. The basis sets used in semi-empirical calculations are specially optimized minimal basis sets composed of Slater-type orbital's [25]. All calculations methods were carried out with the Hyperchem 8 package program. The spectra were interpreted with the aid of normal coordinate analysis based on semi-empirical and ab initio/6-31G** computations by comparison of the band positions and intensities observed in I.R spectra with frequencies and intensities obtained from theoretical calculations. Calculation results using B3LYP/6-31G** and PM3 for thiophene, 3-methelthiophene, polythiophene and poly3-methelthiophene are listed in Table 1.

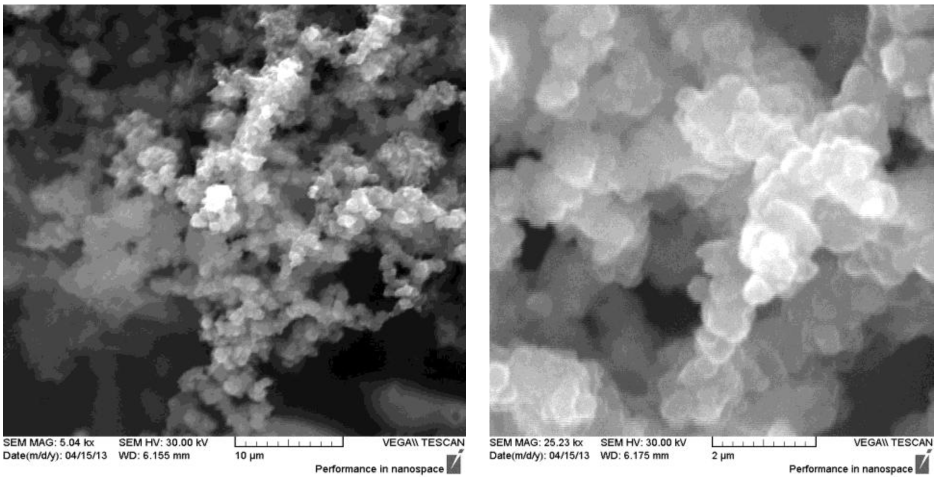

Figure 3. Scanning electrical microscopic images for poly (3-methylthiophene) sample

Table 1. Comparison between calculated and experimental frequencies of the phonon modes in cm^{-1} of thiophene, 3-methelthiophene, non-doped polythiophene and non-doped poly3-methelthiophene.

TH PM3	TH Ab Large(6-31G**	PTH	Asgn	3-MTH PM3	3-MTH Ab Large(6-31G**)	3MTH	P3MTH	Asgn
1B1 382	1B1 484	452	γ_{Ring}	1 A" 200	1 A" 254		435	γ_{R}
1A2 486	1A2 623	476	γ_{Ring}	2 A" 243	2 A" 308	464	455	γ_{R}
1A1 580	1A1 638	580	δ_{C-S}	1 A' 345	1 A' 360	540	486	δ_{R}
1B2 648	1B2 732	738	υc-s	3 A" 382	3 A" 491	594	528	γ_{R}
2A1 713	2A1 780	864	δ_{Ring}	2 A' 517	2 A' 562		570	δ_{C-S}
2B1 724	2A2 824	750	γ_{C-H}	4 A" 562	4 A" 667		567	υ_{R}
2A2 776	2B1 832	785	γ_{C-H}	3 A' 615	3 A' 676	657	621,609[a], 640b	δ_{C-S}
2B2 836	2B2 912		δ_{Ring}	4 A' 726	4 A' 787	682	667,689[c]	$\delta\upsilon_{C-S}$
3A1 1005	3A1 1028		δ_{C-H}	5 A" 759	5 A" 822	763	756,760[d] 701[a],822[e]	γ_{C-H} bending
3B1 918	3B1 1054		δ_{C-H}	5 A' 788	5 A' 836	829	825,830[f]	ν_{C-S}
3A2 966	3A2 1070	1040	δ_{C-H}	6 A" 827	6 A" 896	878	864,791[a] 860[g],835[d]	γ_{C-H} deformation
3B2 1051	4A1 1210	1045	δ_{C-H}	6 A' 940	6 A' 969	929	972, 982[c]	ν_{C-S}
							943, 933[h]	Rocking $(C-H)_3$
4A1 1067	3B2 1214	1225	δ_{C-H}	7 A" 932	7 A" 1055	1033	1010, 1035[e] 1032[i]	δ_{C-H}
4B2 1158	4B2 1396	1171	δ_{C-H}	7 A' 975	7 A' 1109	1080	1093,1036[h]	Rocking $(C-H)_3$
5A1 1308	5A1 1492	1440	υc=c	8 A" 1009	8 A" 1178	1153	1138,1150[j]	C-H Breathing
6A1 1685	6A1 1594	1492	$\upsilon_{C=C}$	8 A' 1048	8 A' 1204		1165	δ_{C-H}
5B2 1781	5B2 1731	1497	$\upsilon_{C=C}$	9 A' 1084	9 A' 1244	1234	1197,1213[d]	twisting $(C-H)_3$ or c-c inter -ring
						1372	1373, 1378[d]	$C_{\alpha}=C_{\beta}$
6B2 3189	6B2 3313		υ_{C-H}	10 A' 1152	10 A' 1390	1384	1296	δ_{C-H}
7A1 3191	7A1 3325		υ_{C-H}	11 A' 1328	11 A' 1485		1438, 1346[k] 1415[f]	$\delta_{C-H} + \upsilon$ c-c
7B2 3204	7B2 3346	3063	υ_{C-H}	12 A' 1379	12 A' 1539	1408	1500,1521[k] 1542[f],1513[c]	$\upsilon_{C\alpha=C\beta}$
							1616,1620[d,l]	
8A1 3212	8A1 3350	3100	υ_{C-H}	13A' 1388	13A' 1607	1539	1640, 1640[b]	$\upsilon_{C\alpha=C\beta}$ Asym stretching
				9 A" 1376	9 A" 1611	1450	1535	$\delta_{(C-H3)}$
				14 A' 1709	14 A' 1628			$\upsilon_{C\alpha=C\beta}$
				15 A' 1809	15 A' 1762	1751	1732	$\upsilon_{C\alpha=C\beta}$ sym stretching
				16 A' 3145	16 A' 3137	2731	2860, 2850[g]	$\upsilon_{(C-H3)}$
				10 A" 3143	10A" 3211	2866	2909, 2922[g]	$\upsilon_{(C-H3)}$
				17 A' 3189	17 A' 3220	2924	2995	$\upsilon_{(C-H3)}$
				18 A' 3190	18 A' 3318		3022	υ_{C-H}
				19 A' 3208	19 A' 3342	3055	3071	υ_{C-H}
				20A' 3215	20 A' 3348	3101	3170	υ_{C-H}

[a]Experimental wave number Ref [42], [b]Experimental wave number Ref [30], [c]Experimental wave number Ref [33], [d]Experimental wave number Ref [35], [e]Experimental wave number Ref [43], [f]Experimental wave number Ref [44], [g]Experimental wave number Ref [45], [h]Experimental wave number Ref [46], [i]Experimental wave number Ref [47],[j]Experimental wave number Ref [48], [k]Experimental wave number Ref [49], [l]Experimental wave number Ref [50]. Abbreviations: ν, stretching; δ, in-plane bending; γ, out of plane.

There is an acceptable correspondence between experimental and theoretical frequencies keeping in mind the limitations of ab initio calculation methods, this vibrational analysis has been made based on the Cs symmetry of methylthiophene group. The PM3 calculated frequencies for thiophene ring fit best with the experimental results.

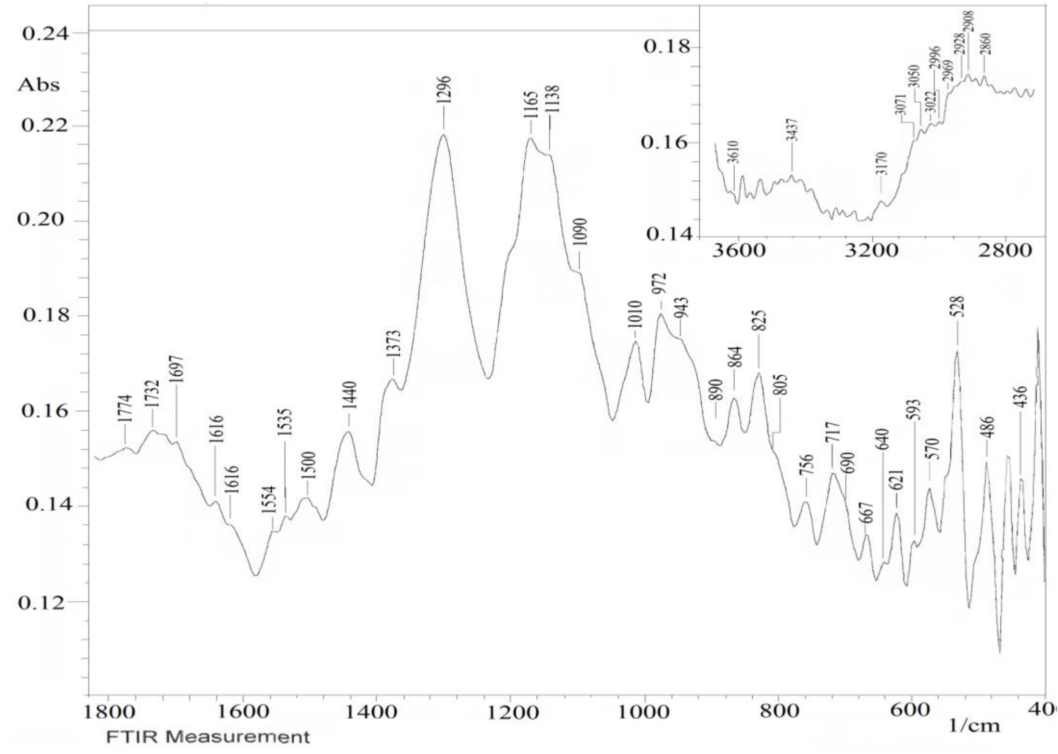

Figure 4. Non-doped poly (3-methelthiophene)

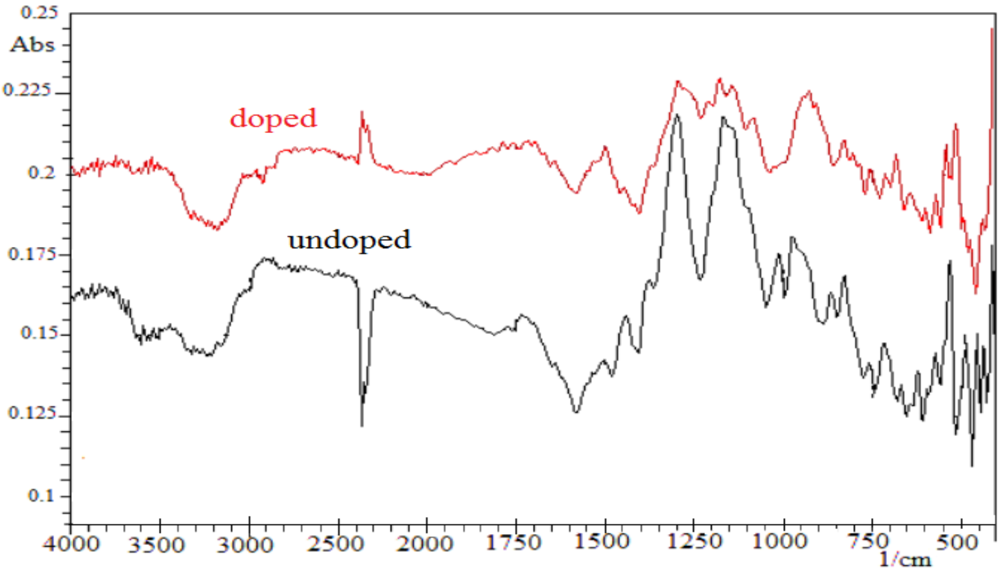

Figure 5. Comparison with doped and non- doped of poly (3-methelthiophene)

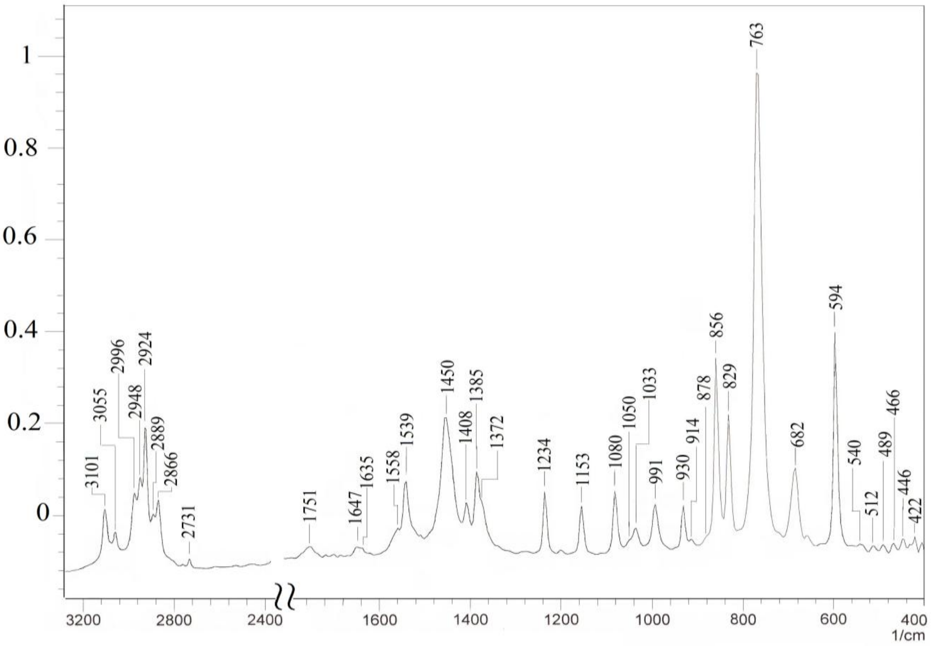

Figure 6. I.R Spectrum of 3-methelthiophene

5. CONCLUSIONS

The present work is devoted to the electrosynthesis of a poly (3-methelthiophene) on gold electrodes and their characterization by the FTIR spectroscopy, which confirms the polymer synthesis by identifying the characteristic absorption bands for this polymer. We applied group theory to determine the normal coordinates of symmetric molecules and to carry out a spectroscopic analysis of their vibrational modes. We have shown that semi-empirical methods are useful qualitative tools for gaining a general overall understanding of the vibrations modes and gives satisfactory interpretation of experimental results. Besides that, we have presented an ab initio and PM3 semiempirical methods to investigate the properties of the conjugated polymer.

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