

*Full Length Research Paper*

# Electrochemical polymerization and Raman study of polypyrrole and polyaniline thin films

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Accepted 4 September, 2012

**In this paper we present thin films of polypyrrole (PPY) and polyaniline (PANI) which have been synthesized electrochemically on Gold electrode by direct oxidation of pyrrole and aniline in Acetonitrile using three electrodes. Raman spectroscopy results were analyzed in terms of normal modes, and spectra were obtained using 633 nm He-Ne laser. It was found that Raman spectra depend on the doping level of PPY and PANi. DFT force field has been calculated at the B3LYP/6-311+ G\* level. General assignments of the vibrational spectra of polypyrrole and polyaniline have been proposed and were compared with those of pyrrole and aniline in order to determine the vibrational modes.**

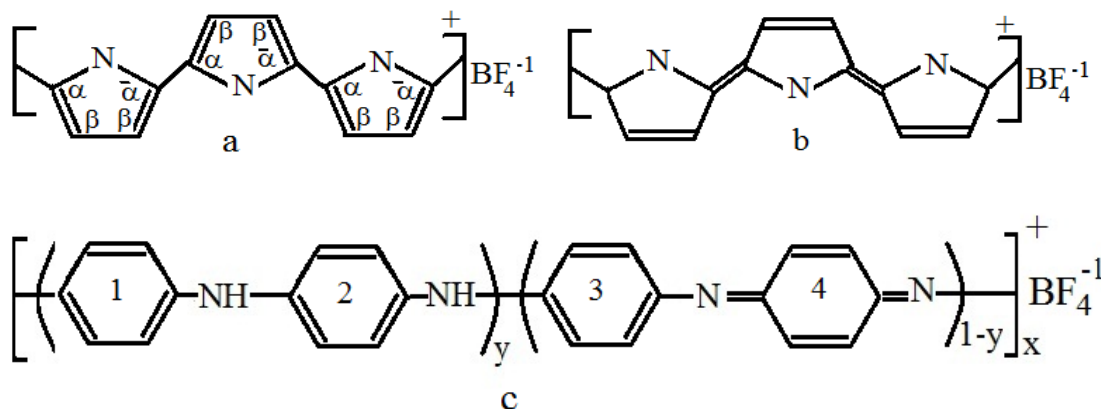
**Key words:** Electropolymerization, polypyrrole, polyaniline, vibrational analysis modes, comparison of DFT functional, Raman spectroscopy.

## INTRODUCTION

Polypyrrole (PPY) and polyaniline (PANI) have been known since the beginning of the last century as conducting polymers. Conductive polymers contain alternating single and double bonds between carbon atoms (conjugation) along the polymer backbone, which makes them semiconductors. These polymers have a good environmental stability and can be easily synthesized, thus giving them a number of interesting properties and making them potentially quite beneficial to use in many commercial applications. PPY and PANi are often used as biosensors (Wei and Ivask, 2006; Zarini et al., 2007), gas sensors (Hosseini et al., 2005; Crowley et al., 2010) and electrochromic windows displays (Metin et al., 2008; Lin and Ho, 2006). They can be synthesized by either oxidative chemical or electrochemical polymerizations of pyrrole and aniline. PPY was chemically synthesized for the first time, in the form of films by Weiss et al. (1967), and electrochemically synthesized by Diaz and Kanazawa (1982), while polyaniline was first synthesized in 1862 (Letheby, 1862), and has been extensively studied as a conducting polymer since the 1980s (Genes et al., 1990), the electrochemical polymerization is one of the excellent methods to synthesize polymers since their area and thickness growth can be controlled. A thin film

polymerized by this method is obtained as an oxidized polymer, such as polypyrrole tetrafluoroborat (Diaz et al., 1982; Wen et al., 2002). It can also be reduced electrochemically to a neutral polymer (Martina et al., 1993; Street et al., 1983). In the past several years these polymers were used to load and release drugs and biomolecules (Entezami and Massoumi, 2006). These polymers can be used for protecting metals from corrosion (Solange, 2007). Polypyrrole has attractive characteristics for use as a radio wave absorbing material (Pouget et al., 1991), and polyaniline was used to produce flexible multi-layer microwave absorbing materials (RAMs) (Jozefowicz et al., 1991).

It is evident that PPY chains are primarily composed of  $\alpha$ - $\alpha'$  linkages of the monomer rings as shown in Figure 1a. All theoretical studies on the electronic Benzoid structures of PPY take these linkages into account (Hotta et al., 1984). However, partial  $\alpha$ - $\beta$  linkages have been mentioned in literature (Street et al., 1983). The polymer has a structure that resembles the aromatic or quinoid forms as seen in Figure 1b (Joo et al., 2001). PANi exists in three stable oxidation states: leucoemeraldine ( $y=1$ ), emeraldine ( $y=0.5$ ), and pernigraniline ( $y=0$ ). Each form can exist in a base form and in various protonated  $H^+$  salt forms. Only the protonated salt form of emeraldine



**Figure 1.** Structure and linkage of Polymers, a) Benzoid form of PPY, b) Quinoid form of PPY, c) Emeraldine form of polyaniline.

is conductive.

Figure 1c shows the basic chemical structure of one repeat unit of PANi (Hennig et al., 1998; Stephen et al., 1998). In each repeat unit there are three benzene rings (denoted 1–3 in Figure 1c) separated by amine (–NH) groups and one quinoid ring (4) surrounded by imine (–N=) groups. For the quinoid ring, which forms double bonds with the nitrogen, there are two pairs of carbon atoms in the ring and four  $\pi$  electrons. Figure 1 shows the structures of these polymers.

Raman Spectroscopy (Schantz et al., 1988; Kim et al., 1995) is an essential and important technique to obtain structural information on conducting polymers such as polypyrrole and polyaniline. Raman spectroscopy is used as a complementary technique to infrared spectroscopy. It provides definite structural characterizations of PPY and PANi because of the characteristic dependence of the Raman spectral pattern on the disposition of the ring constituents of aromatic compounds.

Furukawa et al. (1988) characterized the Raman vibrational modes of PPY at different stages of reduction and assigned the bands to the neutral and radical cation and dicationic species. Bukowska and Jackowska (1990) used *in situ* Raman to study PPY thin films in different electrolytic media. Electrochemically prepared PPY and PANi can be obtained in the shape of freestanding films with good mechanical properties, and their oxidation state is readily controlled in a quantitative manner by electrochemical reduction and oxidation cycles (Tourillon and Garnier, 1982). The structure and properties of PPY and PANi films have been investigated by infrared (IR) and Raman techniques, infrared technique has been mentioned in previous papers (Hasoon, 2010, 2011). In our work we report theoretical calculations of the electronic structures of pyrrole and aniline and their radical cation by using the density functional theory (DFT) (Wang et al., 2011; Wojciechowski and Michalska, 2007; Lopez-Tocon et al., 2001; Ilic et al., 2000), besides the vibrational spectra of Raman of polypyrrole

and polyaniline.

## EXPERIMENTAL SECTION

PPY and PANi films were prepared with thickness range of 1 to 5  $\mu\text{m}$  which can be easily obtained by varying the polymerization time, both monomers were kept under argon. Acetonitrile was used for preparing the electrolytes and the salt used was lithium tetrafluoroborate ( $\text{LiBF}_4$ ). The concentrations for both monomers and salt were 0.1 mL. Argon bubbles deoxygenated the solution prior to electrochemical synthesis. A three-electrode configuration, one compartment cell was used. Both of the working electrode and the counter electrode was a gold foil. A silver electrode was used as reference electrode (Lère–Port et al., 1988), and was connected to the working cell through an  $\text{AgNO}_3$  salt bridge. The potentials of polymerization of pyrrole and aniline were 1 and 1.3 V respectively. We used negative potential (–0.1 to –0.8V) to have a reduced form of polymer. For studying Raman spectra of PPY and PANi, they were recorded on a Labram Aramis Horiba Jobin Yvon with IR<sup>2</sup> option spectrophotometer (He-Ne laser wavelength is 633.5 nm). The microscope lens was a LWD Olympus (X50). The spectral resolution was 1.6  $\text{cm}^{-1}$ .

## GROUP THEORY ANALYSIS

Decomposition of modes of vibration of PPY and PANi will be based on the fact that the point groups of symmetry are the groups  $D_{2h}$  and  $C_s$  respectively, with convention that the Y axis is the axis of the chain (Figure 1). The elements of  $D_{2h}$  group of symmetry are rated as E,  $C_{2z}$ ,  $C_{2y}$ ,  $C_{2x}$ ,  $\sigma_z$ ,  $\sigma_y$ ,  $\sigma_x$ , and I; the elements of  $C_s$  group of symmetry are E,  $\sigma_v$ . In terms of analysis of vibration modes, we must calculate the modes of vibration for monomer and dimer

### Case of PPY

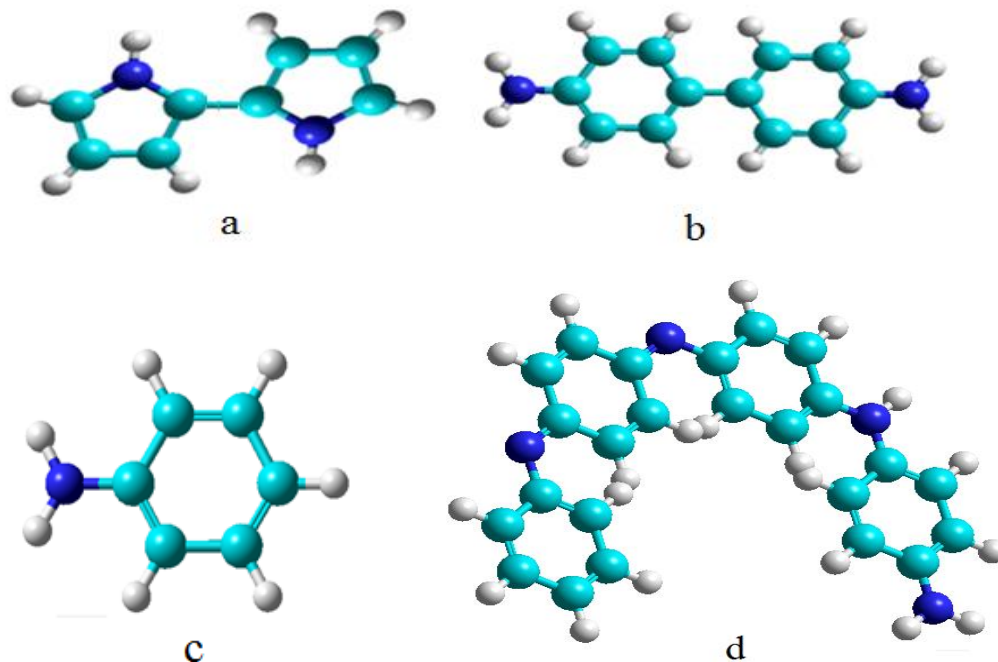
In PPY the ideal lattice contains 16 atoms, so we have 48 degrees of freedom, the order of  $\Gamma$  will be 48 and we can write the 48 irreducible representations of degree 1 of the first Brillouin zone.

In this group of symmetry, the reducible representation (X) and the total numbers of modes ( $\Gamma_{\text{total}}$ ) can be expressed, as shown in Table 1. All the modes are presented in Equation 1.

$$\Gamma_{\text{total}} = 8A_g + 3B_{1g} + 8B_{2g} + 5B_{3g} + 3A_u + 8B_{1u} + 5B_{2u} + 8B_{3u}. \quad (1)$$

**Table 1.** Characters of the irreducible symmetry group  $D_{2h}$ 

$D_{2h}$	E	$C_{2z}$	$C_{2y}$	$C_{2x}$	i	$\sigma_z$	$\sigma_y$	$\sigma_x$
X	48	-4	0	0	0	0	4	16

**Figure 2.** a-Structure of bipyrrole (2, 2-pyrrole), b- Structure of bianiline (4, 4-diamine) c- Structure of aniline, d- Emeraldine structure.

There are 48 modes, this representation contains 3 modes of pure translation ( $Bu_1$ ,  $Bu_2$ , and  $Bu_3$ ), one mode of pure rotation about y-axis ( $B_3g$ ) and 3 modes of  $A_u$  are non active neither in Raman nor in IR, these modes are expressed in Equation 2.

$$\Gamma_{vib} = 8A_g + 3B_1g + 8B_2g + 4B_3g + 7B_1u + 4B_2u + 7B_3u \quad (2)$$

There are 23 active modes in Raman, ( $8A_g + 3B_1g + 8B_2g + 4B_3g$ ).

### The vibration of the hydrogen atoms

The vibrations of elongation, and the deformations in the plane and deformations out of plane links C-H are, ( $A_g + B_2g + B_1u + B_3u$ ),  $A_g$  and  $B_2g$  active in Raman, are located at  $3000 \text{ cm}^{-1}$ . The representation caused by deformations of C-H in the plane are, ( $A_g + B_2g + B_1u + B_3u$ ), and those in Raman is  $A_g + B_2g$ . The representation caused by deformation of C-H out of plane are, ( $B_1g + B_3g + A_u + B_2u$ ), So  $B_1g + B_3g$  are active in Raman. Therefore, we have 6 modes of vibration active in Raman for the Hydrogen's vibration. Also we have 6 modes of (N-H) vibrations three of these modes, ( $1A_g + 1B_2g + 1B_3g$ ), are active in Raman and ( $1B_1u + 1B_2u + 1B_3u$ ), are active in infrared.

### Ring vibrations

It was found that there are 9 modes of vibration for pyrrole ring,

each of these modes has two degrees of freedom for polypyrrole unit cell, the symmetry group of pyrrole ring is  $C_{2v}$ , the irreducible representations, represented by Equation (3)

$$\Gamma_{total} = 5A_1 + 3A_2 + 2B_1 + 5B_2 \quad (3)$$

There are a total of 9 modes of vibration, as represented by Equation (4)

$$\Gamma_{vib} = 4A_1 + 1A_2 + 1B_1 + 3B_2 \quad (4)$$

### Application of group theory to polymer

If we take the bipyrrole as shown in Figure 2(a), this dimer have  $C_{2h}$  group symmetry, so the total number of modes can be expressed as shown in Equation (5), and the total number of modes of vibrations can be represented by Equation (6)

$$\Gamma_{total} = 10A_g + 5A_u + 5B_g + 10B_u \quad (5)$$

$$\Gamma_{vib} = 10A_g + 4A_u + 4B_g + 8B_u \quad (6)$$

We can transfer these modes of vibrations to  $D_{2h}$  group symmetry, which is more symmetrical, so the 10 modes of  $A_g$  for bipyrrole under the data sheet of the table of  $D_{2h}$  group symmetry turn to  $10A_g \rightarrow 5B_{2g} + 5A_g$ . Similarly for other modes  $4A_u \rightarrow 2B_{1g} + 2B_{3g}$ ,  $4B_g \rightarrow 2A_u + 2B_{2u}$ . In addition,  $8B_u \rightarrow$

**Table 2.** The irreducible characters of  $D_{2h}$  symmetry group.

$D_{2h}$	E	$C_{2z}$	$C_{2y}$	$C_{2x}$	i	$\sigma_z$	$\sigma_y$	$\sigma_x$
X	78	-6	0	0	0	0	6	26

$\nu_4B_{1u}+4B_{3u}$ .

The rings vibrations and the movement of all rings are shown in more detail in Equations (7) and (8), respectively.

$$4A_g+1B_{1g}+3B_{2g}+1B_{3g}+1A_u+3B_{1u}+1B_{2u}+4B_{3u} \quad (7)$$

$$1A_g+1B_{1g}+2B_{2g}+1B_{3g}+1A_u+1B_{1u}+1B_{2u} \quad (8)$$

There are still another type of vibration, which is the relative vibration between the two half's of the ring. Therefore, one mode of  $B_{1g}$  of translation in OZ direction, corresponding to (C-C) vibration occurs around 1000 to 1100  $\text{cm}^{-1}$ , while one mode of  $B_{2g}$  of translation in OY direction, and one mode ( $B_{3g}$ ) of translation in OX direction, both vibrate are at low frequency.

#### Case of bianiline (4, 4-diamine structure)

The bianiline ideal lattice contains 26 atoms, as shown in Figure 2b, so we have 78 degrees of freedom and we can write the 78 irreducible representation of degree 1 of the first Brillouin zone. This model can be considered as a  $D_{2h}$  symmetry group, the reducible representation (X) and the total numbers of modes ( $\Gamma_{\text{total}}$ ) can be expressed in Table 2 and the irreducible representations are expressed by Equation (9).

The irreducible representations can be expressed in Equation 9:

$$\Gamma_{\text{total}} = 13A_g+5B_{1g}+13B_{2g}+8B_{3g}+5A_u+13B_{1u}+8B_{2u}+13B_{3u} \quad (9)$$

The calculation shows that we have 72 modes of vibration as shown in Equation 10

$$\Gamma_{\text{vib}}=13A_g+4B_{1g}+12B_{2g}+7B_{3g}+5A_u+12B_{1u}+7B_{2u}+12B_{3u} \quad (10)$$

The modes active in Raman in this symmetry group are  $13A_g$ ,  $4B_{1g}$ ,  $12B_{2g}$  and  $7B_{3g}$ .

#### The vibration of the carbon-hydrogen (C-H) and Nitrogen-Hydrogen (N-H) atoms

The 24 modes of vibrations of elongation, deformations in the plane and deformations out of plane that link C with H in C-H Bond are  $2A_g+2B_{2g}+2B_{1u}+2B_{3u}$ ,  $2A_g+2B_{2g}+2B_{1u}+2B_{3u}$  and  $2B_{1g}+2A_u+2B_{3g}+2B_{2u}$ , respectively.

Similarly, we have 12 modes of vibrations of elongation, deformations in the plane and deformations out of plane that link N with H in N-H bond,  $1A_g+1B_{2g}+B_{1u}+B_{3u}$ ,  $1A_g+1B_{2g}+B_{1u}+B_{3u}$  and  $1B_{1g}+1B_{3g}+1A_u+B_{2u}$ , respectively.

#### Ring vibrations for aniline bianiline

The symmetry groups of aniline ring and bianiline rings are  $D_{6h}$  and  $C_{2h}$ , respectively. It was found that there are 12 modes of vibrations for aniline ring and 30 modes of vibrations for bianiline rings; these 30 modes are  $11A_g+4B_g+5A_u+10B_u$ . Finally, we have 6 modes of vibrations of elongation, deformations in the plane and

deformations out of plane that link C with N in C-N bond,  $1A_g+1B_u$ ,  $1A_g+1B_u$  and  $1B_g+1A_u$ , respectively.

#### The case of polyaniline (Emeraldine structure)

The molecule of aniline ( $C_6H_5NH_2$ ) as shown in fig (2c) is composed of 26 atoms, since this molecule belongs to the  $C_s$  point group of symmetry, this group is a poor one and have only two elements of symmetry (S and E), and we have 42 Irreducible representations and 36 modes of vibrations. All these fundamental modes are both infrared (IR) and Raman active and can be expressed in Equation 11

$$\Gamma_{\text{vib}}=20A'+16A'' \quad (11)$$

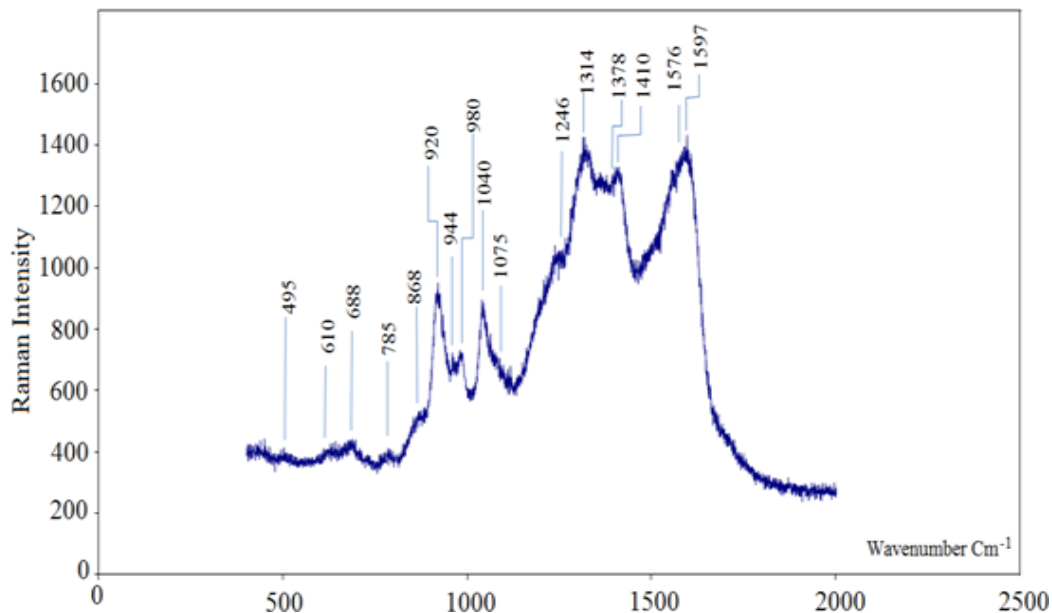
These 36 modes of vibrations include  $15(9A'+6A'')$  modes of C-H vibrations,  $6(3A'+3A'')$  modes of N-H vibrations,  $12(7A'+5A'')$  modes of Ring vibrations and finally 3 modes of C-N vibrations, some of these vibrations are listed in Table 2.

Similar calculations for the case of emeraldine structure ( $C_{24}H_{20}N_4$ ) as shown in Figure (2d), which has also a  $C_s$  group symmetry, result in 138 modes of vibrations that are active in both IR and Raman as shown in Equation 12.

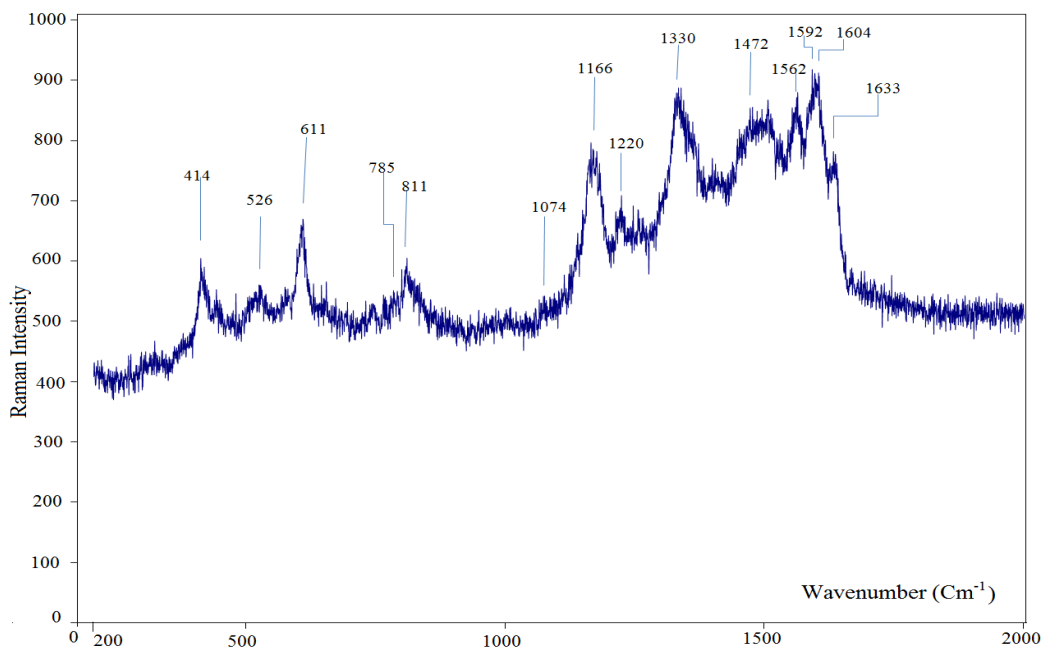
$$\Gamma_{\text{vib}}=93A'+45A'' \quad (12)$$

## RESULTS AND DISCUSSION

To characterize the studied PPY and PANi films in this work we first recorded the resonance Raman (RR) spectrum (Figure 3 and 4, respectively), and also presented a theoretical analysis of the vibrational normal modes by using the hyperchem 8 package to precise prediction and assignment of vibrational modes. Both experimental and calculated frequencies of PPY and PANi are tabulated in Table 3 and 4. Figure 3 depicts the most important peak ( $A_g$ ) is at  $1597 \text{ cm}^{-1}$  which represents C = C symmetry stretching and another peak ( $B_{2g}$ ) located at  $1576 \text{ cm}^{-1}$  (Liu et al., 2000; Gongcalves et al., 2000; Liu et al., 2008; Grzeszczuk et al., 2010). The two peaks of ( $A_g$ ), located at  $1314$  and  $1378 \text{ cm}^{-1}$  assigned to be the inter-ring (C-C) stretching (Crowley and Cassidy, 2003; Santos et al., 2007). The vibration at  $1246$ ,  $1047$  are attributed to a ring deformation mode ( $\delta$  ring) $A_g$ , (Gongcalves et al., 2000; Grzeszczuk et al., 2010), and the two bands at  $944$  and  $980 \text{ cm}^{-1}$  for  $A_g$  and  $B_{3g}$  types, respectively are assigned to ring deformation associated with dication (dipolaron) and radical cation (polaron) respectively (Crowley and Cassidy, 2003; Santos et al., 2007; Kathuroju and



**Figure 3.** Raman spectrum for polypyrrole film.



**Figure 4.** Raman spectrum for polyaniline.

Jampana, 2011). The charge carriers in this type of polymers are spin less, it's suggested that these are bipolarons; singlet bound states of two positively charged polarons. The polaron levels, introduced due to doping in the band gap, such that a given conjugated chain segment could carry only one charge. The band with double peaks at 1040 (Ag) and 1075 (B2g)  $\text{cm}^{-1}$  is

attributed to the C-H in-plane deformation (Liu et al., 2000; Hernandez et al., 1999). Finally the intensity and frequency of some modes of vibrations vary from one sample to another depend on the method of synthesis, the quality of dedoping and defects substituting the rings of the polymer structure.

The resonance Raman spectrum of polyaniline thin film

**Table 3.** Comparison of some experimental wave number ( $\text{cm}^{-1}$ ) of modes in Raman spectrum for Polypyrrole thin films and theoretical harmonic frequencies in  $\text{cm}^{-1}$  for pyrrole, bipyrrrole.

Pyrrole freq (RM1)	Pyrrole freq. (B3LYP/6-11+G*)	Bipyrrrole Freq. (Ab initio/ 6-311+G*)	PPY observed $\omega$	Pyrrole calculated $\omega^g$	PPY Expt <sup>a</sup>	Assignment
3332 A1	3624 A1	3700 Ag		3530		$\text{U}_{\text{N-H}}$
3188 A1	3230 A1	3336 Ag		3134		
3177 B2	3221 B2	3318 Ag		3113		
3158 A1	3209 A1	3307 Ag				$\text{U}_{\text{C-H}}$
3154 B2	3201 B2					
1796 B2	1677 B2	1879 Ag				$\text{U}_{\text{C=C}}$
1687 A	1611	1724 Ag 1641 Ag	1597	1536	1571-1590	$\text{U}_{\text{C=C}}$ $\text{U}_{\text{C-C}}$
1714 B2	1605 B2	1475 Ag	1410	1421	1405 <sup>b</sup>	$\text{U}_{\text{C-N}}$
1336 A1	1228 A1	1392 Ag	1314, 1378	1380	1331-1386	Breathing
1313 B2	1339 B2	1328 Ag	1220		1215-1218 <sup>c</sup>	$\delta_{\text{N-H}}$
1175 B2	1209 B2	1213 Ag	1246, 1047			$\delta_{\text{Ring}}, \delta_{\text{-H}}$
1092 B	1095 B2	1182 Ag	1040, 1075	1040	1035-1083 <sup>d</sup>	$\delta_{\text{C-H}}$
1063 A1	992 A1	974 Ag	944, 980		932 <sup>e</sup> , 975	$\delta_{\text{Ring}}$
784 B1	681 B1	923 Bg	868-920	824	875-930 <sup>f</sup>	
867 B1	815 B1	844 Bg		723		$\gamma_{\text{C-H}}$
916 A2	845 A2					
809 A2	649 A2	765 Bg	785			$\gamma_{\text{Ring}}$
457 A1	582 A2					
647 B1	587 B1	636 Bg		643		$\gamma_{\text{Ring}}$
317 B1	457 B1	319 Bg		477		$\gamma_{\text{N-H}}$

<sup>a</sup>Experimental wave number (Liu and Hwang, 2000), <sup>b</sup>Experimental wave number (Kim et al., 2007), <sup>c</sup>Experimental wave number (Koo et al., 2011; Crowley and Cassidy, 2003; Liu, 2004), <sup>d</sup>Experimental wave number (Kim et al., 2007; Lee et al., 2010), <sup>e</sup>Experimental wave number (Furukawa et al., 1988; Liu et al., 2000), <sup>f</sup>Experimental wave number (Crowley and Cassidy, 2003; Santos et al., 2007), <sup>g</sup>Frequencies,  $\omega$  ( $\text{cm}^{-1}$ ) (Geidela and Billes, 2000). Abbreviations:  $\nu$ , stretching;  $\delta$ , in-plane bending;  $\gamma$ , out of plane.

deposited at a gold electrode is shown in Figure 4, the type of movement and symmetry of most frequencies is given in Table 4. This figure contains most of Raman bands, characteristic for PANi and its derivatives, which corresponds to the spectrum of the typical emeraldine base (EB) form of PANi (Sedenkova et al., 2008; Ciric-Marjanovic et al., 2008). This spectrum contains the most markers for PANi bands, located at 1604 and 1592  $\text{cm}^{-1}$  corresponding to carbon-carbon single and double band stretching vibrations in benzene and quinone type rings, respectively (Celly et al., 2009; Do Nascimento et al.,

2008). We also observe specific bands of C=N stretching modes of imine located at 1472  $\text{cm}^{-1}$  and C-N stretches of amine sites at 1220  $\text{cm}^{-1}$  (Lapin et al., 2010). The stretching vibrations of an intermediate bond C~N<sup>+</sup> are seen in Raman spectra with characteristic frequency around 1330  $\text{cm}^{-1}$  (Figure 4), and a literature publication does not agree on the exact value of this frequency (Bober et al., 2011; Bilal et al., 2011; Mazeikiene et al., 2010). The band located at 1562  $\text{cm}^{-1}$  is characteristic of N-H bending vibrations (Mazeikiene et al., 2010), whereas C-H in plain deformation mode of is

**Table 4.** Comparison of some experimental wave number ( $\text{cm}^{-1}$ ) of modes in Raman spectrum for polyaniline thin Films and theoretical harmonic frequencies (in  $\text{cm}^{-1}$ ) for aniline, bianiline.

Aniline (RM1)	Aniline B3LYP/6-311+G*	Bianiline Ab initio/6-31G**	PANi observed $\omega$	Aniline calculated freq. $\omega^m$	PANi expt <sup>h</sup>	Assignment
1796 A'	1739 A'	1844 Ag 1682 Ag	1633 1592	1637 1624 1696 <sup>n</sup> 1665 <sup>n</sup> 1627 <sup>o</sup> 1608 <sup>o</sup>	1618 1578	$\nu_{\text{C}=\text{C}}$ (B ring) $\nu_{\text{C}=\text{C}}$ (B&Q ring)
1520 A'	1475 A'	1662 Ag  1646 Ag	1604  1472	1609 1649 <sup>n</sup>  1332 <sup>n</sup>	1615 <sup>i</sup>  1480 <sup>i</sup> 1463 <sup>j</sup>	$\nu_{\text{C}-\text{C}}$ (B Ring)  $\nu_{\text{C}=\text{N}}$ (imine)
1611 A'	1560 A'	1533 Ag	1562	1624	1564 <sup>k</sup>	$\delta_{\text{N}-\text{H}}$ (semi-Q)
1717 A'	1688 A'	1616 Ag	1220	1279 1271 <sup>o</sup>	1220 <sup>k,l</sup>	$\nu_{\text{C}-\text{N}}$ (amine)
1260 A'	1348 A'	1152 Ag	1166	1161 1185 <sup>n</sup> 1176 <sup>o</sup>	1163 1165 <sup>k</sup>	$\delta_{\text{C}-\text{H}}$ (semi-Q)
1157 A'	1139 A'	1256 Ag				$\delta_{\text{N}-\text{H}}$
1178 A'	1177 A'	1070 Ag	1074	1089 <sup>n</sup>	1076 <sup>k</sup>	$\delta_{\text{C}-\text{H}}$ (B)
955 A''	927 A''	928 Bg	878	943 <sup>n</sup>	883	$\nu_{\text{C}-\text{H}}$ (B&Q ring)
861 A''	806 A''		811	808 <sup>n</sup>	815	$\delta_{\text{C}-\text{c}}$ (B Ring)
1004 A'	956 A'	864 Ag		860 <sup>n</sup> 994 <sup>o</sup>	997 <sup>l</sup>	Breathing
879 A'	825 A'	750 Ag	785	759 <sup>n</sup>	788 <sup>j</sup>	$\delta_{\text{Ring}}$ (Q Ring)
627 A'	629 A'	683 Ag	743	652 <sup>n</sup>	750 <sup>j</sup>	$\delta_{\text{Ring}}$ (imine and amine)
529 A'	537 A'	512 Ag	611		632 <sup>j</sup>	$\delta_{\text{Ring}}$ (B Ring)
521 A''	435 A''	670 Bg	526	621 <sup>n</sup>		$\nu_{\text{N}-\text{H}}$

<sup>h</sup>Experimental wave number (Arsov et al. (1998), <sup>i</sup>Experimental wave number (Wang et al., 2011), <sup>j</sup>Experimental wave number (Lapin et al., 2010), <sup>k</sup>Experimental wave number Ref (Bober et al., 2011; Mazeikiene et al., 2010), <sup>l</sup>Experimental wave number (Bober et al., 2011), <sup>m</sup>Frequencies,  $\omega$  ( $\text{cm}^{-1}$ ) Ref (Wojciechowski and Michalska, 2007), <sup>n</sup>Frequencies,  $\omega$  ( $\text{cm}^{-1}$ ) (Lopez-Tocon et al., 2001), <sup>o</sup>Frequencies,  $\omega$  ( $\text{cm}^{-1}$ ) (Ilic et al., 2000). Abbreviations: B, benzenoid ring; Q, quinoid ring or benzene ring with quinoid character;  $\nu$ , stretching;  $\delta$ , in-plane bending;  $\gamma$ , out of plane.

quinonoid observed around  $1166 \text{ cm}^{-1}$  (Rozlivkova et al., 2011; Qingli et al., 2010). Some other vibration modes should be noted, for PANi Films, the band located at  $785 \text{ cm}^{-1}$  corresponds most probably to quinine ring deformation vibrations (Giusca et al., 2002). Furthermore, other bands in the Spectrum are located around 743 and  $811 \text{ cm}^{-1}$ , which correspond probably to imine site deformation vibrations and amine deformations (Mazeikiene et al., 2010; Qingli et al., 2010).

In order to obtain the optimized vibrational frequencies, theoretical calculations have also been carried out by applying the DFT calculations based on HF and Becke3-Lee-Yang-Parr (B3LYP) level with 6 311+G\*basis set, we also employed (RM1) the semi-empirical methods for electronic molecular structure modeling. These calculations were performed in order to determine and understand the physical origin of the fundamental modes of vibration of the molecules of aniline, bianiline, pyrrole

and bipyrrrole. These calculated values were used to interpret the experimentally obtained from Raman scattering bands. Theoretical *Ab initio* calculations have also been carried out at HF level adopting 6-311+G\* as the basis set. Even though considerable literature already exists that describe the semi-empirical molecular orbital, density functional (DFT) (Ilic et al., 2000; Biswas and Umapathy, 2000; Fu-Qiung et al., 2004). As seen from Tables 3 and 4, the calculated optimized vibrational frequencies, viz C-N, C-C, C=C, N-H, and C-H, from B3LYP/6-311+G\* are in good agreement with the experiment. Overman et al. (2005) found that the frequency situated at 1007 cm<sup>-1</sup> can be interpreted as breathing pyrrole ring, from theoretical calculations using RM1 and DFT methods, we found that this type of breathing frequency is located at 1336 and 1228 cm<sup>-1</sup> respectively. For the case of bipyrrrole this frequency is located at 1392 cm<sup>-1</sup> (using *Ab initio* calculations).

## Conclusions

In this paper we study the theoretical predictions of results of spectroscopy based on the theory of groups, the study was carried out to understand; what are the elements of the spectra of monomers that must be found in the spectra of polymers. The films have been successfully synthesized by electrochemical polymerization by using certain amount of Pyrrole and Aniline monomers, these films were investigated at a fixed potential of 1.1 and 1.3 V with various monomer ratios respectively. Calculations by group theory of these polymers gave as 23 and 38 modes active in Raman (Ag, Bg) for Polypyrrole and Polyaniline (4, 4-diamine), respectively. An attractive feature of the oxidized conducting form of polypyrrole and polyaniline is that they are stable in air relative to many other conducting polymers. The calculations of fundamental frequencies by (B3LYP) level with 6-311+G\* basis have been performed for investigating the vibrational spectra. The Raman spectrum of neutral polypyrrole shows six major bands at 1600, 1575, 1320, 1376, 955, and 990 cm<sup>-1</sup>. These bands are assigned to modes of pristine polypyrrole. Similarly, we interpreted the vibrational tapes observed in polyaniline at 1623, 1595, 1466, 1267, 1564, 1168, 788, 748 and 812 cm<sup>-1</sup>. This vibrational analysis made it possible to provide the foundations of a good comprehension of the vibrational properties of polyaniline. This work demonstrates that Raman spectroscopy is a useful method to determine the neutral-polaron-bipolaron transitions in conducting polymers.

## ACKNOWLEDGMENTS

The author would like to thank the Ecole Nationale supérieure de chimie de Montpellier in France (ENSCM)

specially Pr J.P Lère-Porte for helping us in the measurements of Raman spectra. This study was also supported by a grant from College of Science for Women, University of Baghdad.

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