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## The correlation between density functional theory (DFT) and spectroscopic investigations of PVA/PVP nanocomposites containing gold nanoparticles.

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### ABSTRACT

Films of polymer nanocomposites based on polymer blend of polyvinyl alcohol (PVA)/ polyvinyl pyrrolidone (PVP) loaded by different contents of gold nanoparticles was prepared using casting method. The correlation between theoretical investigation using spectroscopic density functional theory (DFT) and experimental techniques by X-ray diffraction and Fourier transform infrared (FT-IR) spectroscopy. IR bands of C=O stretching and C=C bending (at about  $1441\text{ cm}^{-1}$ ) is attributed to semi-crystalline nature of PVA/PVP polymer blend as obtained from X-ray results. The estimated forms from DFT and FT-IR spectra show the main characteristic bands of PVA/PVP blend in their positions while PVP adsorbed the nanogold at the surface preferably via the non-bonding electrons of the carbonyl group. Scanning electron microscopy (SEM) images show that the prepared gold nanoparticles were mono dispersed within the PVA/PVP polymeric matrices.

**Keywords:** PVA/PVP; Nanoparticles; DFT; X-ray; FT-IR.

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## INTRODUCTION

In recent years, there has been an enormous amount of research on improving the physical and chemical properties of polymeric and glassy amorphous materials by blending, functionalizing and doping with nano-particles [1]. Combined Density Functional Theory (DFT) with spectroscopic tool (FT-IR) will be used to characterize virgin and nanoparticle doped samples of the same nominal composition. The structure and mechanism of reaction is the first step for suggesting the possible method of doping and obtained properties for specified applications

Molecular dynamics and density functional theory (DFT) [2, 3] calculations will be tested to model orbital energies of samples (amorphous materials as well as crystalline materials yet discrepancy between theory and experiment exist.

Here we have got a bent to guage a series of relatively easy calculation ways victimization the standard Gaussian 09 code package and/or Material Studio [4, 5]. Chain length saturation square measure getting to be determined for homo- and donor-acceptor kind materials whereas, HOMO energy could also be related to experiment [6].

Polymer blends play an important role because of their relatively simple preparation methods and diverse resulting properties [7]. The blends with enhanced attributes are created by blending at least two polymers to consolidate their properties for specific purposes [8].

Polyvinyl alcohol (PVA) is the most widely produced water soluble synthetic polymer over a wide range of temperatures depending on its level of hydrolysis, sub-atomic weight and inclination to hydrogen bond in aqueous solutions [9]. PVA has been found to have a variety of applications in the industrial sector and it has been attractive in different areas of science and technology [10, 11].

Polyvinylpyrrolidone (PVP) has attention among as conjugated polymer; due to its well environmental stability, easy processability and good physical properties. It's abroad wide selectionsof applications like electrochemical devices (batteries, displays) [12]. The PVA/PVP blend may be a potential material having a charge storage capacity and dopantdependentelectrical properties. Their interactions have been delineating in several papersdue to the interesting properties of the resulting blend, that mix the option ofeach polymers [13, 14]. The utilization of modifiers will modification the properties of PVA/PVP mix in several aspects. However, it's necessary to stay in mind the initial plan of application and in keeping with that select the acceptable filler [15].

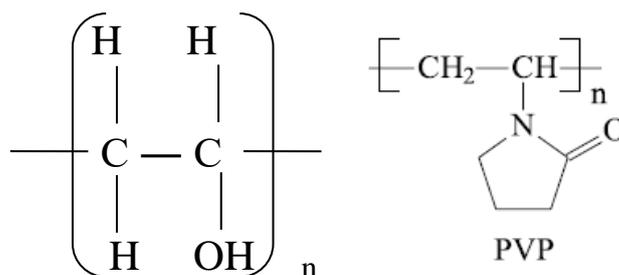
The main goal of the current work is to prepare some films of pure PVP/PVP polymer blend and alsothe blend loaded by gold nanoparticles to correlate experimental (FT-IR) results with theoretical approach(DFT) to know the character of interaction between PVA/PVP blend and the dopant nanoparticles and extended to analysis thechanges in its physical parameters.

## EXPERIMENTAL WORK

### Sample preparation

Poly (vinyl alcohol) (PVA) is one of the basic materials used to produce the blend, which was obtained from E-Merck (Germany) in the style of crystals with the following structure as shown in scheme (1). The molecular weight of PVA polymeric matrix is nearly 14,000.

Polyvinyl pyrrolidone (PVP) is supplied by SISCO Research Laboratory Ltd. (Mumbai, India) which was obtained principally by radical chemical change in resolution with peroxide or azobisisobutyronitrile (AIBN) as initiator. PVP is soluble in water and insolution; t has wonderful wetting properties and promptly forms films. PVP is in the form of a white powder with molecular formula:  $(C_6H_9NO)_n$  and the structure as shown in scheme (2).



**Scheme (1): PVA structure; Scheme (2): PVA structure**

Equal amounts of PVP and PVA (50/50) by weight/weight were added to double distilled water with stirring at room temperature to complete dissolution until a suitable viscous solution is formed. The viscous solution was loaded with various quantities of pre-prepared gold nanoparticles. The samples were prepared according to:

$$w(\text{wt. \%}) = \frac{w_g}{w_g + w_b} \times 100 \quad (1)$$

where  $w_g$  and  $w_b$  represent the weights for the gold nanoparticles and the blend, respectively. To prepare pure blend and filled polymeric films, the viscous solution was poured onto cleaned glass Petri dishes and dried in an oven at 40 °C for 3 days to ensure removal of the solvent traces. After drying, the films were peeled from Petri dishes and kept in vacuum desiccators until use. The films were cut into suitable pieces for measurements. The thickness of the obtained films was in the range of 0.02-0.03 mm.

### Characterization Techniques

The X-ray diffraction scans were obtained using PANalytical X'Pert PRO XRD system using Cu  $K\alpha$  radiation (where,  $\lambda = 1.540 \text{ \AA}$ , the tube operated at 30 kV, the Bragg's angle ( $2\theta$ ) in the range of 5-50°). In this analysis, the peak locations ( $2\theta$ ) in X-ray diffraction spectra are used to identify the different crystalline structures in the pure and doped films. The FT-IR absorption spectra were carried out for different films using the single beam Fourier transform-infrared spectrometer (Nicolet iS10, USA) at room temperature. FT-IR spectra of the samples were obtained in the spectral range of 4000-400  $\text{cm}^{-1}$  to study their structures. The UV/VIS absorption spectra were measured in the wavelength region of 190-1100 nm using a spectrophotometer (JASCO 630, Japan) to study the change in structures of the samples due to adding the fillers and their optical properties. The morphology of the films was characterized by scanning electron microscope using (Quanta FEG 250), operating at 30 kV accelerating voltage. Surface of the samples were coated with a thin layer of gold (3.5 nm) by the vacuum evaporation technique to minimize sample charging effects due to the electron beam.

## RESULTS AND DISCUSSION

### X-ray diffraction analysis

To obtain some information about the structural and the crystallite of the prepared samples under investigations, the X-ray diffraction scans were studied.

Figure (1a-c) represents the X-ray diffraction scans of pristine PVP, PVA and PVA/PVP blend, respectively. As we see in this figure, there are peaks (small peaks) observed at  $2\theta \approx 12.2^\circ$ ,  $2\theta \approx 13.6^\circ$  and the sharp peak centered at  $2\theta \approx 20^\circ$ . This at  $20^\circ$  corresponds to (110) reflection [16, 17], which is consistent with the values in the standard card (JCPDS file No. 41-1049). Also, the two peaks are observed at  $2\theta \approx 10.1^\circ$  and  $18.1^\circ$  assigned to pure PVP [18].

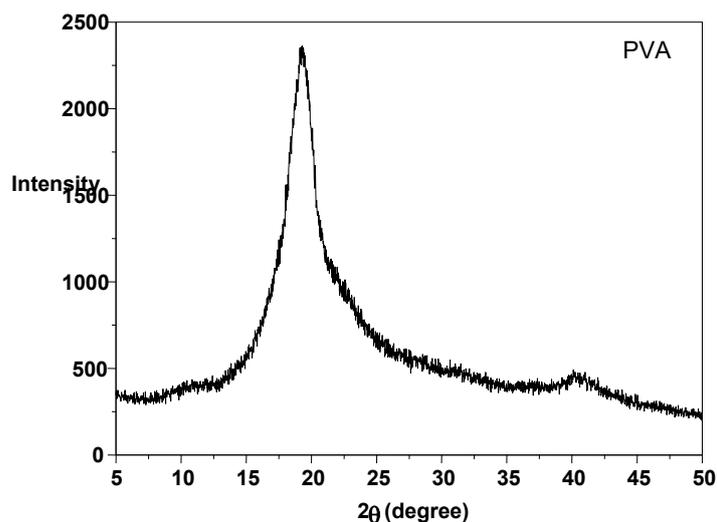


Figure (1.a): The X-ray diffraction of PVP

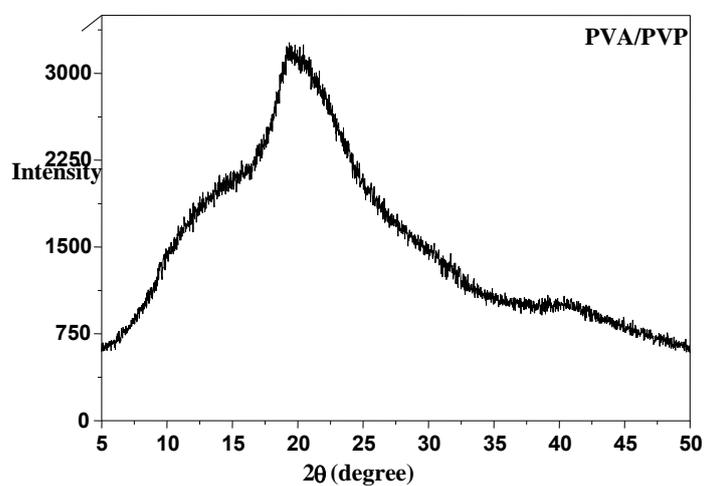


Figure (1b): The X-ray diffraction of PVA.

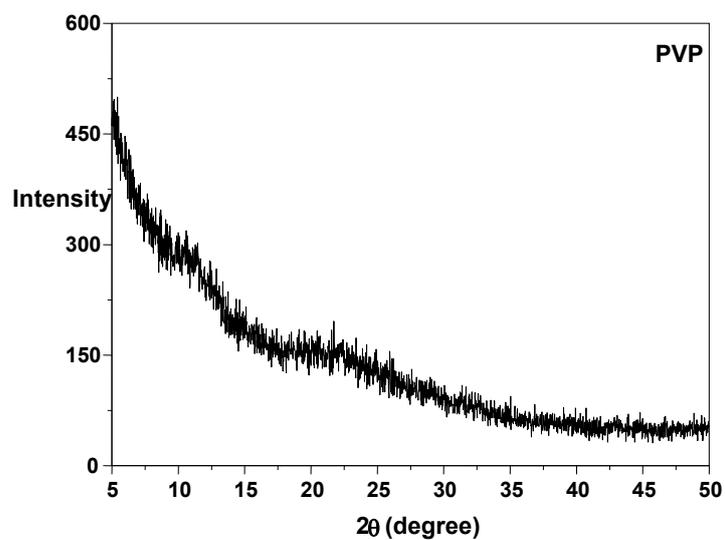


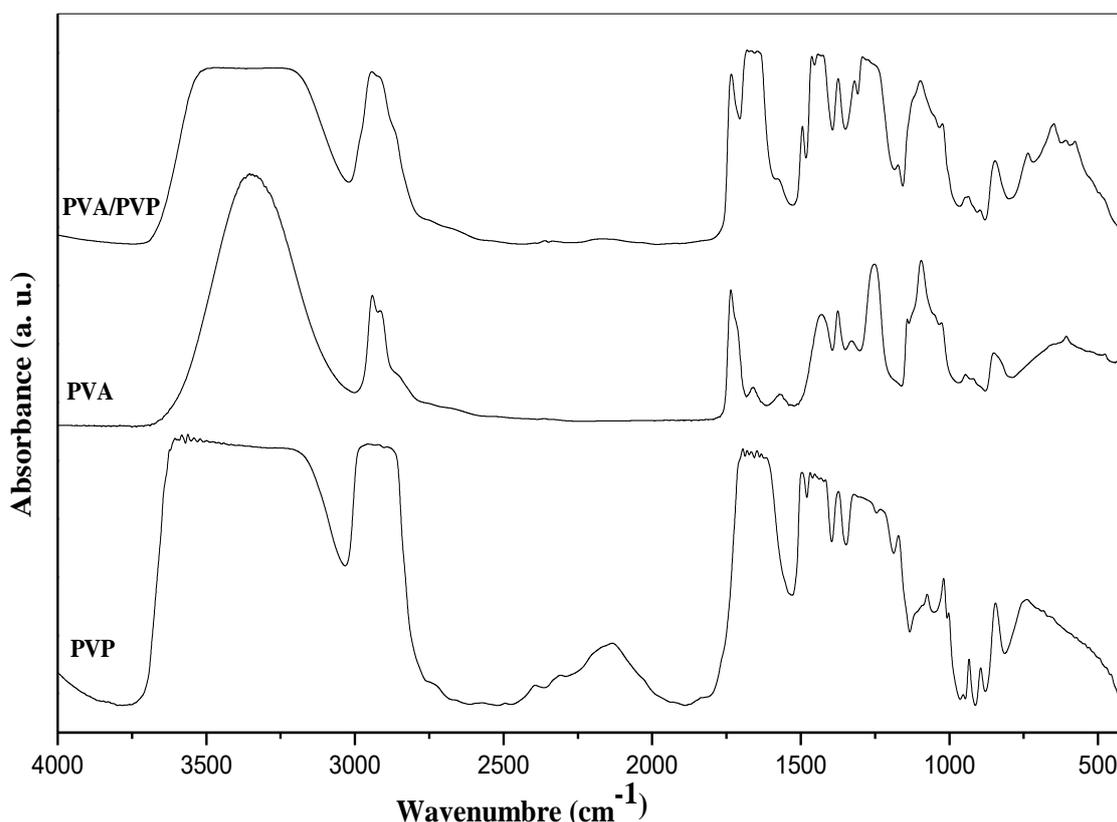
Figure (1c): The X-ray diffraction of (PVA/PVP) polymer blend

**Fourier transform infrared analysis**

The FT-IR spectroscopy has been proven to be a very powerful technique to detect the intermolecular interaction between the polymer blend and its interaction with fillers.

Figure (2) shows FT-IR absorption spectra of pristine polymers and PVA/PVP blend recorded at room temperature in the region 4000-400  $\text{cm}^{-1}$ . The spectra exhibited characteristic bands of stretching and bending vibrations of the functional groups formed in the prepared films. FT-IR absorption bands positions and their assignments of the prepared samples are listed in Table (1).

From the spectra, the broad band at about 3455  $\text{cm}^{-1}$  is assigned to the stretching vibration of hydroxyl group (OH) of PVA, which may be due to the intermolecular or intramolecular type of hydrogen bonding of the blend. The band corresponding to  $\text{CH}_2$  asymmetric stretching vibration occurs at about 2933  $\text{cm}^{-1}$ . The band at about 1096  $\text{cm}^{-1}$  correspond1s to C–O stretching of carbonyl groups present on the PVA backbone [19]. The vibrational band at about 1647  $\text{cm}^{-1}$  corresponds to C=O stretching of PVA and/or PVP [20]. It is remarkable that; the present double bonds segments are considered as suitable sites for polarons and/or bipolarons. On the other hand, very small absorption band at about 1539 $\text{cm}^{-1}$  is assigned to the characteristic vibration of C=N (pyridine ring) of PVP [21]. The FT-IRband observed at 962  $\text{cm}^{-1}$ is corresponding out-of-plane rings C–H bending. The absorption band appearing at 1441  $\text{cm}^{-1}$  is assigned to C=O stretching and C=C bending is attributed semicr-ystalline nature of the polymer blends as we see in X-ray analysis.



**Figure 2: The FT-IR spectrum of pure PVP and pure PVA and blend (PVA/PVP).**

**Table 1: FT-IR absorption bands positions and their assignments of the prepared samples**

Vibrational frequency ( $\text{cm}^{-1}$ )	Band assignment
3380	O–H stretching
2950	( $\text{CH}_2$ ) asymmetric stretching

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1740	C=O stretching
1620	C=C stretching
1463	O–H bending
1440	C=C (pyridine ring)
1377	CH <sub>2</sub> bending
1304	C–H wagging
1094	C–O stretching
840	C–C stretching

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**Scanning electron microscopy**

Figure (3) shows the SEM images of the surface morphology for PVA, PVP and their blends. It is determined that just about the prepared samples are clear and homogeneous. It is observed that, pure samples have a uniform surface morphology with a rather smooth surface. Whereas the polymer blend is more uniform. There are some semi-tori with different sizes appeared as bright spots with different degree of roughness for other samples.

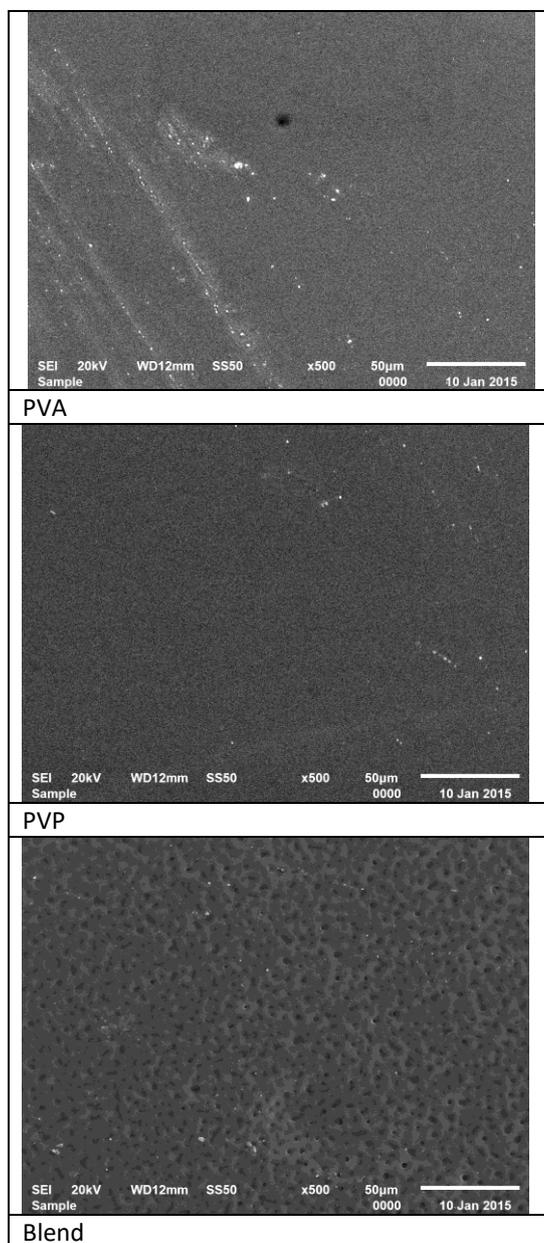
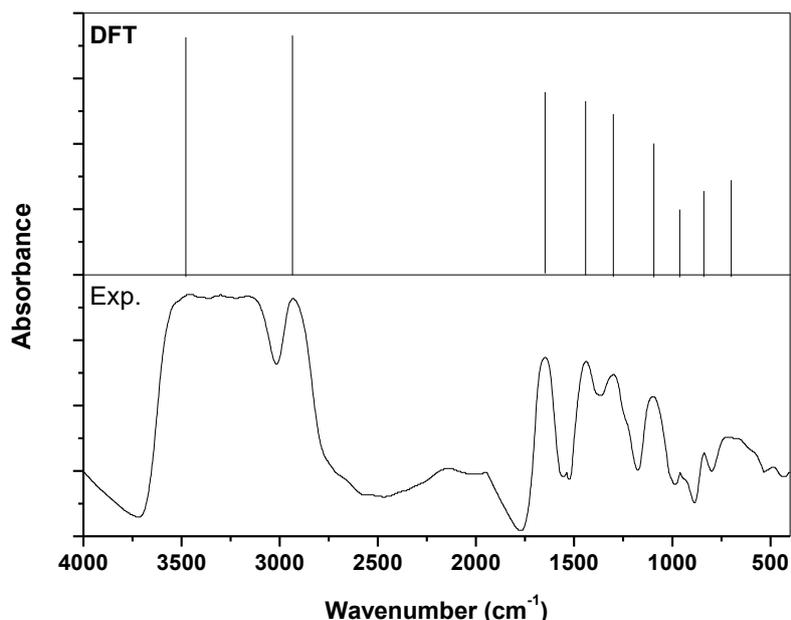


Figure 3: SEM images of (a) PVA, (b) PVP and (c) Polymer Blend.

### Density Functional Theory (DFT) calculations

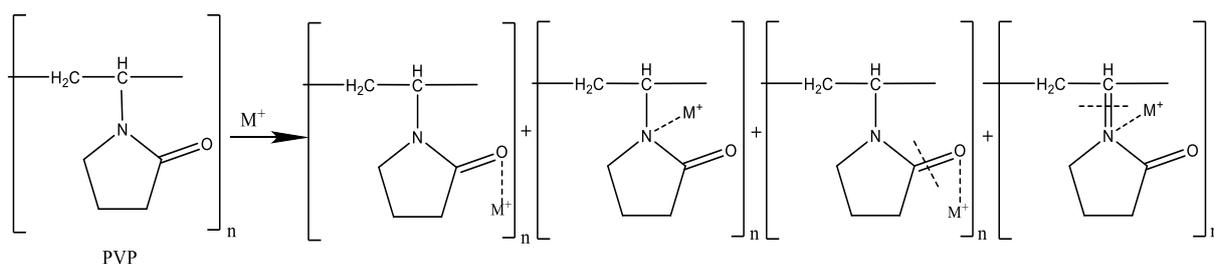
The calculations for density functional theory (DFT) are study by DMOL3 programing Materials Studio. The DFT calculations are estimated using double numerical basis sets with polarization functional(DNP) and this set isrelated to Gaussian6-31G programming. Some studiesshowed that the DNP sets aremore accurate than Gaussian sets. TheRPBE functionalis the best exchange–correlationfunctional, based on the generalized gradient approximation is take place of some exchange and correlation effects of electrons. The geometric optimization is performed without any symmetry restriction.

Every point in DFT theoretical data has characterized by harmonic frequency calculationsat every level and the FT-IR active harmonic frequencies have been identified and compared as seen in Figure (4).



**Figure 4: Experimental and DFT result of suggested structure**

There are 4 kinds of probabilities of achemical interaction between poly vinyl alcohol and polyvinyl pyrrolidoneas observed in Figure (5).



**Figure 5: Models of the interaction between PVP with M=PVA.**

Figure (6) illustrates the optimized chemical structure form which obtained from DFT determinations. The form shows that the structure may be more stabilized usingchemical interactions with oxygen atoms in polypyrrolidone, and this is related to the experimental spectrum of FT-IR, also, the structure reveals that nitrogen atom has a weak interaction. So, we see that, the four model for the chemical interaction are found to be possible whileusingother probabilitieswhich represented from experimental data (from IR spectra) and from theoretical chartusing DFT [19].

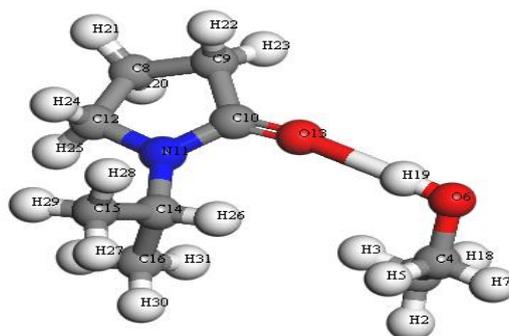


Figure 6: Optimized structure for PVA/PVP chemical interaction

### Chemical reactivity:

In the atrical quantum mechanics, the calculations of chemical energies for HOMO ( $\pi$ -donor) and LUMO ( $\pi$ -acceptor) are used as parameters. In HOMO, the  $\pi$ -orbital give the donor electron while in LUMO, the  $\pi$ -orbital give an acceptor electron [22]. These  $\pi$ -orbital are called the frontier molecular orbitals (FMOs) [19]. The discussion of these chemical energies as the following: i) The negative values of  $E_{\text{HOMO}}$  and  $E_{\text{LUMO}}$  and their neighboring orbitals indicate the stability of PVA/PVP pure blend as we see in Figure (7), ii) The HOMO and LUMO overlap is a governing factor in various reactions. So, the orbitals of the monomer with the largest value of molecular orbital coefficients can be considered as the sites of coordination as shown in Figure (8) and iii) The energy band gap between  $E_{\text{HOMO}}$  and  $E_{\text{LUMO}}$  is very stable and its used to study and investigate the chemical interactions and kinetic stability of the molecule. This molecule has a little energy gap with more polarized and interacted than hard ones because they easily offer electrons to an acceptor. Furthermore, the little values of energy band gap attributed to the groups entering into conjugation in those soft molecules [22].

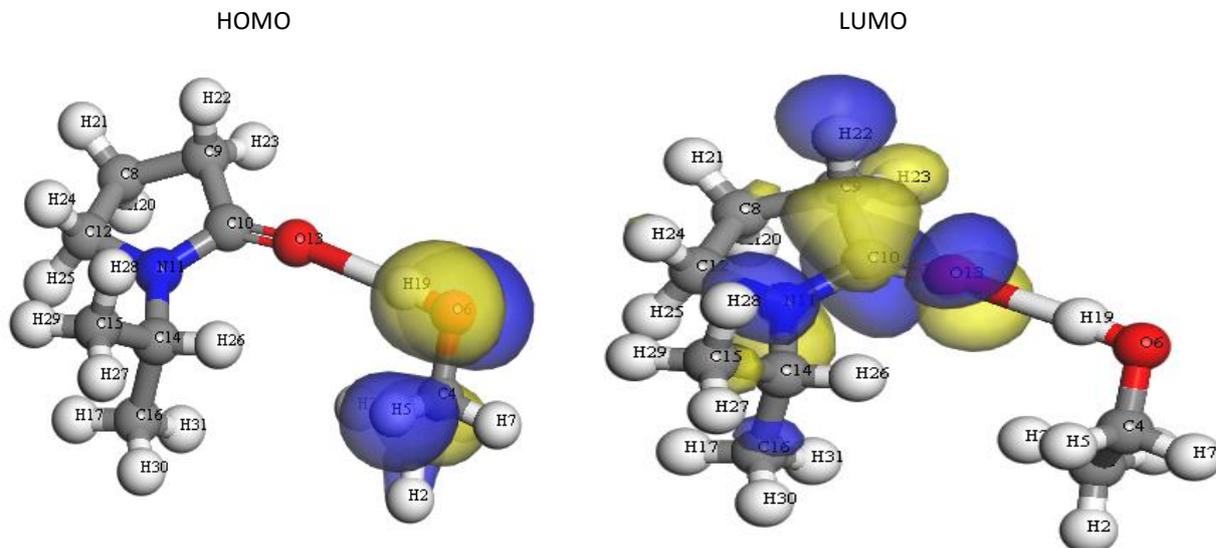


Figure 7: HOMO/LUMO of Optimized structure PVA/PVP.



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