

## Solvent Effect On Electronic Transitions, Ph Effect, Theoretical Uv Spectrum, Homo Lumo Analysis Of 2,4-Dihydroxy-5-Fluoropyrimidine

Richa Sharma<sup>1</sup>, B.S Yadav<sup>2</sup>

<sup>1</sup>Venketeshwara University, Gajraula, U.P (India)

<sup>2</sup>D.N.PG College, Meerut, U.P (India)

---

**Abstract:** The present study deals with the solvent effect on the electronic spectra of 2,4-dihydroxy-5-fluoropyrimidine i.e, the effect of polar solvents are ethanol, methanol, and water has been studied on the electronic transitions of the title molecule both experimentally and theoretically. The homo lumo analysis has been studied. Theoretical calculations are made with the help of Gaussian 03 by using HF and density functional theory DFT/B3LYP with complete relaxation using 6-31++G(d,p) basis set. The variation of pH also has been discussed. The mulliken charges have been computed and discussed.

**Keywords:** 2,4,5 DHFP; UV spectrum, HOMO-LUMO, pH effect, Mulliken charge.

---

### I. Introduction

Fluorinated heterocyclic compounds are becoming increasingly important in many areas including the pharmaceutical industry, material science and agriculture.[1]. The spectral interpretation of N-heterocyclic compounds like pyrimidine, cytosine, thymine, uracil and their derivatives is difficult because of their high complexity and low symmetry. The characterization of free base molecule is very useful for the understanding of specific biological processes[2] and in the analysis of relatively complex systems. Nitrogen heterocyclic compounds play an important role in the structure and properties of nucleic acids[3]. The compounds containing fluorine are very important as the molecules containing fluorine may also exhibit hydrogen bonding. The substantial functional changes in physicochemical [4] and biological properties of organic compounds become due to the presence of fluorine. Incorporation of fluorine into drug molecules can affect their physicochemical properties like bone strength, rate of metabolism, pharmacological properties such as toxicology[5]. The important information regarding charge transfer within the molecule and important quantum chemical parameters are calculated and discussed. All calculations which support the assignments are made by using HF and DFT methods. The charge distribution over all the molecules i.e. mulliken charges have been discussed.

### Experimental Details:

Spec-pure grade of 2,4-Dihydroxy-5-fluoropyrimidine was obtained from Aldrich Chemie U.S.A. Its purity was confirmed by elemental analysis and melting point (282°C) determination. The ultraviolet spectrum in water, methanol, ethanol were recorded on a Beckman M-35-UV-Visible spectrophotometer. Vapour phase ultraviolet spectra were tried on medium Quartz spectrograph but even under best experimental conditions no reportable bands were observed. Attempts to record ultraviolet spectra in non-polar solvents such as carbontetrachloride, chloroform and benzene failed.

### II. Result And Discussion

The structural diagram of the compound is given in Fig(1). The intermolecular and intra molecular hydrogen bonding in 2,4,5DHFP is shown in Fig(2). Hydrogen bonding by the solvent is shown in Fig(2). The near ultraviolet absorption spectra of 2,4,5 DHFP in polar solvents i.e. ethanol, methanol, water has been shown in Fig(4) and Table(1). The effect of pH variation with the change of solution concentration, on electronic transitions in water, methanol and ethanol for the compound are presented in Fig(5,6,7) also with concentration. Ultraviolet absorption spectral data for the compound under study is shown in Table.3.1. Theoretical ultraviolet absorption data for the compound under calculation shown in Table (2) and (3) using HF/6-31++(d,p) and DFT /6-31++(d,p). The Homo Lumo analysis of said compound are shown in Fig (7) and (8) and Table (5) under calculations. The mulliken charge distribution is shown in Fig (9) and data is shown in Table(4) respectively.

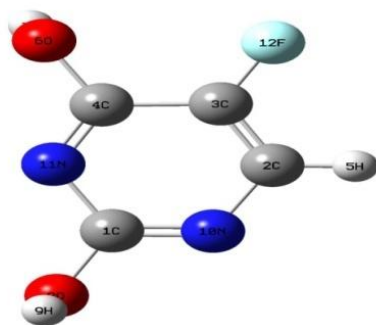


Fig1: Molecular structure of 2,4-dihydroxy-5-fluoropyrimidine

### Effect of solvents on electronic transitions of 2,4,5 DHFP

Whenever a substituent (either acidic and basic) such as  $-OH$ ,  $-SH$  and  $-NH_2$  etc is present in nitrogen heterocyclic acid base and tautomeric equilibria are likely to occur in dilute solution which may cause a shift in the  $n-\pi^*$  and  $\pi-\pi^*$  transitions. The polar solvents and those which can form hydrogen bonds tend to interact electrostatically with various chromophores[6]. This changes due to the charge distribution in the molecule and result in increased delocalization. For  $\pi-\pi^*$  transitions both the ground and excited states are stabilised and absorption towards longer wavelengths[7]. For  $n-\pi^*$  transitions, the ground state in hydrogen bonding involves only one electron of lone pair, the other having been promoted to an upper energy level. The hypsochromic shift with increasing solvent polarity i.e. ethanol  $\rightarrow$  methanol  $\rightarrow$  water is a useful means of recognising  $n-\pi^*$  transitions. During the present study also  $n-\pi^*$  transition and  $\pi-\pi^*$  transition both are blue shifted with increasing solvent polarity.

In the title compound hydrogen bonding by the solvent is formed. The fluorine acts as a proton acceptor[8], and electronic interactions between the lone pair of electrons of the fluorine group and electrons of the ring is decreased, leading to a hypsochromic shift[9]. This possibility is arise due to the decrease in electron density on the atom. The greater effective size of the group may result in twisting it out of plane of the aromatic ring[10]. It is evident that the greater the possibility of hydrogen bonding by the solvent, the greater the hypsochromic shift or vice versa. Thus increasing dielectric constant of solvent, which increases the ionising potentiality [11] of the solute molecules. However, solvation may also be partly due to hydrogen bonding of the solvent [12]. This results that hypsochromic shift observed in the title compound on going from ethanol to water. After correlation of experimental and theoretical data we find that theoretical calculated wavelengths are approximately as same as experimental values.

### Effect of pH

According to Mason et al. [13] With a decrease in acid concentration or with an increase in pH a bathochromic shift occurs in quinolines. Lord and Thomson[14] also reported a definite bathochromic shift in aqueous solutions with increasing solution of pH of uracil and adenine derivatives. In the title compound a decrease in solution concentration in water, methanol and ethanol, causes an increase in pH, resulting in a bathochromic shift which is apparent from Fig.

As suggested by Cumper et al[15] when hydrogen bonding by the solvent dominates over that by the solute, there is a hypsochromic shift so that it results there will be a smaller bathochromic shift in those solvents in which there is a greater possibility of hydrogen bonding by the solvent. Due to the high polarity and Protic nature of water[16]. There is a greater possibility of hydrogen bonding in water as compared with ethanol and methanol. In the case of the said compound a decrease of solution concentration produces a greater bathochromic shift in methanol and ethanol when compared with the water as increase in pH.

### HOMO LUMO Analysis

The highest occupied molecular orbital(HOMO) acts as an electron donor while the lowest unoccupied molecular orbital(LUMO) acts as an electron acceptor. To exemplify the chemical reactivity and kinetic stability of the molecules, the homo lumo analysis has been made. The energy gap of homo lumo explains the eventual charge transfer interaction[17] within the molecule, which is also very important for the biological activity[18] of the molecule. The global softness and hardness of compound indicates increases and decreases the movement of the system towards a more or less stable configuration[19,20]. The large energy gap implies the high stability of the compound while small energy gap indicates the low stability of the compound[21]. In the title compound the global softness is more in DFT than HF.

**Mulliken Charge**

Mulliken charges provide a mean of estimating partial atomic charges from calculation, particularly those based on the linear combination of atomic orbitals[22,23]. Mulliken charges help to rationalize observed chemical behaviour of atoms. It can show the large spurious change as the molecular configuration is changed. Atomic charges play an important role in quantum chemistry[24]. The behaviour of certain classes of molecules, which do not confirm to classical pattern of ionic, covalent and coordination of hydrogen bonding[25] components are explained by Mulliken charge transfers. In the title compound both fluorine and nitrogen atom consist negative charges both in HF and DFT methods which shows the intramolecular interaction in solid form.

**Table 1: Experimental absorption data of 2,4-dihydroxy-5-fluoropyrimidine**

| Solvent  | DC*  | RI**   | Assignments and corresponding Wavelength<br>$\lambda$ (nm) |             |               |
|----------|------|--------|--|-------------|---------------|
|          |      |        | n- $\pi^*$   | $\pi-\pi^*$ | n- $\sigma^*$ |
| Ethanol  | 25.0 | 1.3773 | -  | 243<br>270  | -             |
| Methanol | 32.0 | 1.3362 | 322  | 206         | -             |
| Water    | 80.5 | 1.3380 | 333  | 196         | -             |

\*Dielectric constant

\*\*Refractive index

**Table 2: Theoretical absorption data of 2,4-dihydroxy-5-fluoropyrimidine using HF/6-31++G(d,p)**

| Excited levels  | CI Expansion Coefficient | Excitation Energy | Wavelength $\lambda$ (nm) | Oscillation Strength |
|-----------------|--------------------------|-------------------|---------------------------|----------------------|
| Ethanol         |                          |                   |                           |                      |
| Excited State 4 |                          |                   |                           |                      |
| 32→35           | 0.11519                  | 4.9554            | 250.20                    | 0.0044               |
| Excited State 5 |                          |                   |                           |                      |
| 31→37           | -0.20461                 | 5.8004            | 213.75                    | 0.0896               |
| 33→36           | 0.10013                  | -                 | -                         | -                    |
| Excited State 6 |                          |                   |                           |                      |
| 30→37           | -0.13681                 | 6.2671            | 197.83                    | 0.0007               |
| 32→37           | -0.22171                 | -                 | -                         | -                    |
| Methanol        |                          |                   |                           |                      |
| Excited State 4 |                          |                   |                           |                      |
| 32→35           | 0.11416                  | 4.9650            | 249.72                    | 0.0043               |
| Excited State 5 |                          |                   |                           |                      |
| 31→37           | -0.20440                 | 5.8084            | 213.75                    | 0.0881               |
| 33→36           | 0.10672                  | -                 | -                         | -                    |
| Excited State 6 |                          |                   |                           |                      |
| 30→37           | -0.13629                 | 6.2710            | 197.71                    | 0.0007               |
| 31→37           | -0.22181                 | -                 | -                         | -                    |
| Water           |                          |                   |                           |                      |
| Excited State 4 |                          |                   |                           |                      |
| 32→35           | 0.11121                  | 4.9831            | 248.81                    | 0.0043               |
| Excited State 5 |                          |                   |                           |                      |
| 31→37           | -0.20340                 | 5.8220            | 212.96                    | 0.0897               |
| 33→36           | -                        | -                 | -                         | -                    |
| Excited State 6 |                          |                   |                           |                      |
| 30→37           | 0.13525                  | 6.2697            | 197.75                    | 0.0008               |
| 31→37           | 0.22198                  | -                 | -                         | -                    |

**Table 3: Theoretical absorption data of 2,4-dihydroxy-5-fluoropyrimidine using DFT/6-31++G(d,p)**

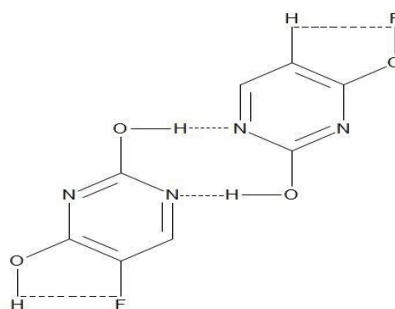
| Excited Level            | CI Expansion Coefficient | Excitation Energy | Wavelength $\lambda$ (nm) | Oscillation Strength |
|--------------------------|--------------------------|-------------------|---------------------------|----------------------|
| Ethanol                  |                          |                   |                           |                      |
| Excited State 4<br>33→34 | 0.68922                  | 4.4029            | 280.61                    | 0.0043               |
| Excited State 5<br>33→35 | 0.67453                  | 4.6052            | 269.23                    | 0.0002               |
| Excited State 6<br>31→35 | 0.24985                  | 4.8897            | 253.56                    | 0.0727               |
| 32→34                    | 0.60684                  | -                 |                           |                      |
| Methanol                 |                          |                   |                           |                      |
| Excited State 4<br>33→34 | 0.68920                  | 4.4094            | 281.18                    | 0.0042               |
| Excited State 5<br>33→35 | 0.67452                  | 4.6109            | 268.89                    | 0.0002               |
| Excited State 6<br>31→35 | 0.25119                  | 4.8955            | 253.26                    | 0.0714               |
| 32→34                    | 0.60655                  |                   |                           |                      |
| Water                    |                          |                   |                           |                      |
| Excited State 4<br>33→34 | 0.68922                  | 4.4203            | 280.49                    | 0.0042               |
| Excited State 5<br>33→35 | 0.67456                  | 4.6211            | 268.30                    | 0.0002               |
| Excited State 6<br>31→35 | 0.25118                  | 4.9053            | 252.75                    | 0.0727               |
| 32→34                    | 0.60736                  | -                 |                           | -                    |

**Table 4: Mulliken Charges of Atoms**

| Atoms | HF/6-31++G(d,p) | DFT/6-31++G(d,p) |
|-------|-----------------|------------------|
| 1C    | 0.497033        | 0.313133         |
| 2C    | 0.131772        | 0.079243         |
| 3C    | 0.274046        | 0.338703         |
| 4C    | 0.455234        | 0.239557         |
| 5H    | 0.259595        | 0.236739         |
| 6O    | -0.612092       | -0.534635        |
| 7H    | 0.485475        | 0.470160         |
| 8O    | -0.621654       | -0.535297        |
| 9H    | 0.482839        | 0.465458         |
| 10N   | -0.430074       | -0.336871        |
| 11N   | -0.489786       | -0.385359        |
| 12F   | -0.432389       | -0.350830        |

**Table 5: HOMO LUMO Analysis of 2,4-dihydroxy-5-fluoropyrimidine**

| Parameters           | HF/6-31++G(d,p) | DFT/6-31++G(d,p) |
|----------------------|-----------------|------------------|
| $E_{\text{HOMO}}$    | -0.38430        | -0.28123         |
| $E_{\text{LUMO}}$    | 0.04300         | -0.06845         |
| Energy Gap           | 0.4333          | 0.2127           |
| Chemical Potential   | -0.16765        | 0.17484          |
| Global Hardness      | 0.21665         | 0.10635          |
| Electronegativity    | 0.16765         | -0.17487         |
| Global softness      | 4.61573         | 9.40214          |
| Ionisation Potential | 0.38430         | 0.28123          |

**Fig2: Intermolecular and Intra molecular Hydrogen Bonding in 2,4-Dihydroxy-5-Fluoropyrimidine**

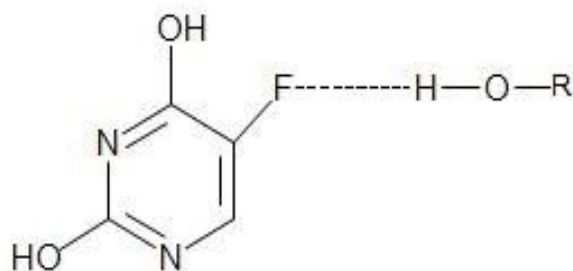


Fig3: Hydrogen Bonding by the Solvent in 2,4-dihydroxy-5-Fluoropyrimidine

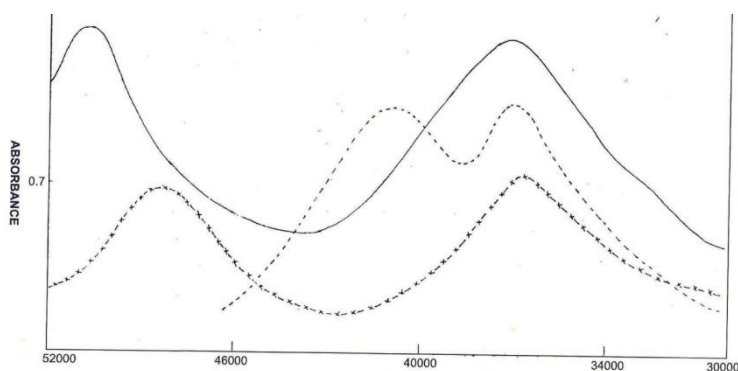


Fig4: Ultraviolet Absorption spectra of 2,4-Dihydroxy-5-fluoropyrimidine in water(-), methanol(-x-x) and ethanol(----)

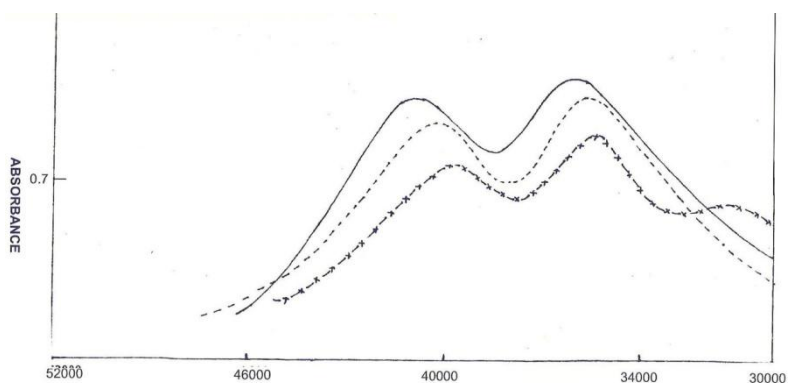


Fig5: Ultraviolet absorption spectra of 2,4-Dihydroxy-5-fluoropyrimidine in Ethanol at concentration.0010%(-), .0005%(---) and .00025%(-x-x)

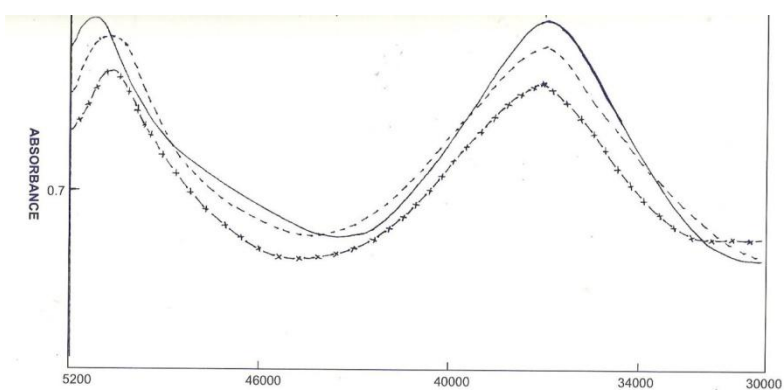


Fig6: Ultraviolet Absorption Spectra of 2,4-Dihydroxy-5-Fluoropyrimidine in Water at concentration .0010%(-), .0005%(---), and .00025%(-x-x)

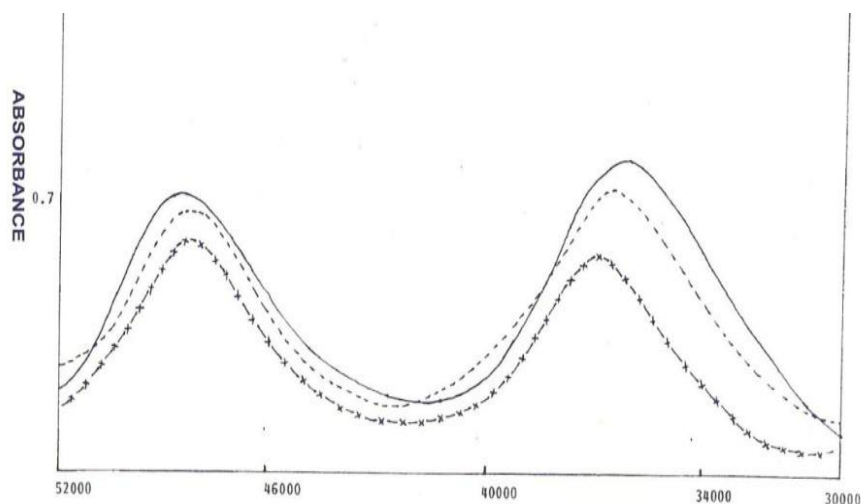


Fig7: Ultraviolet Absorption spectra of 2,4-Dihydroxy-5-fluoropyrimidine in Methanol at concentration .0010%(-), .0005%(- -) and .00025%(-x-x)

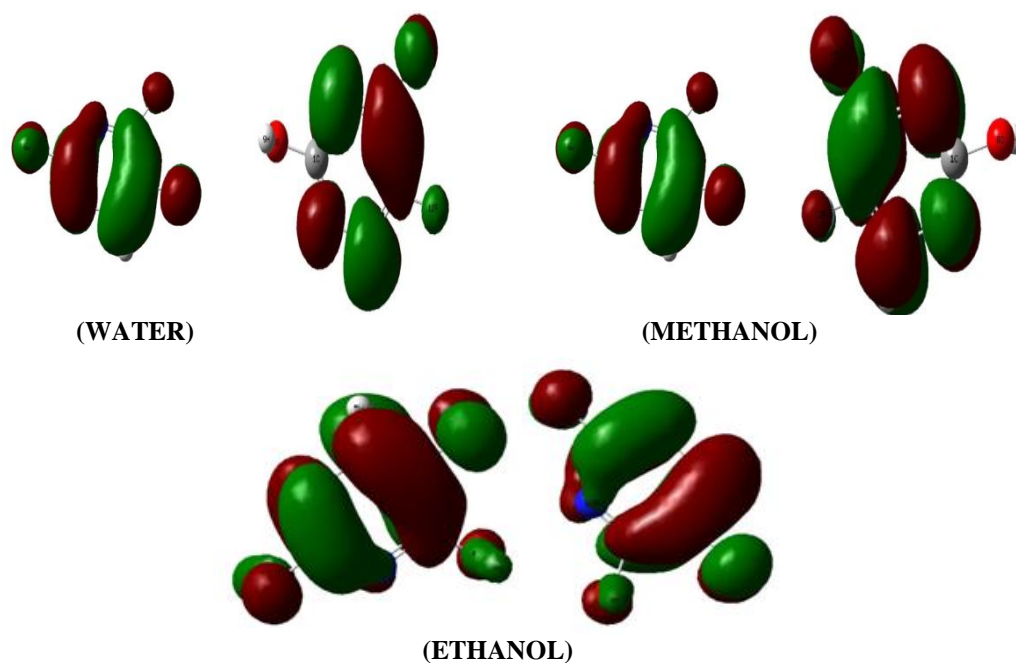
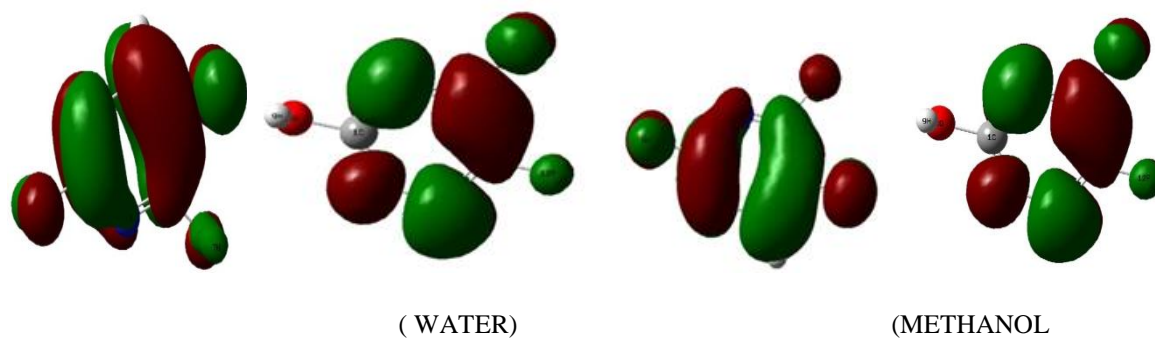
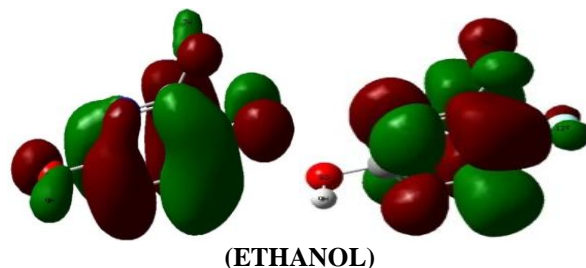
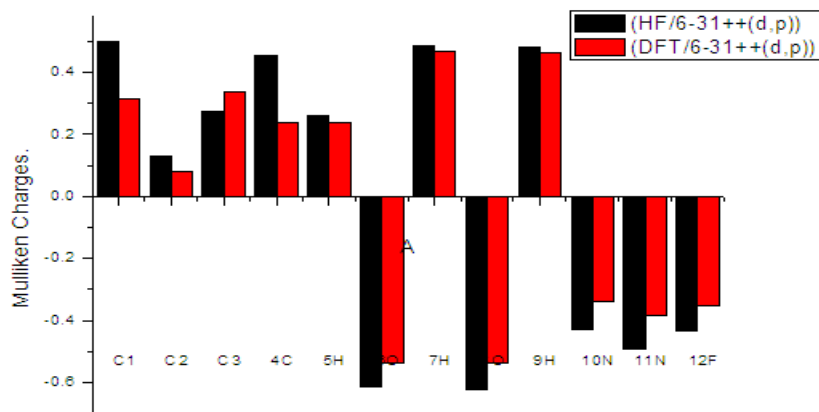


FIG8: HOMO LOMO Images of 2,4-Dihydroxy-5-fluoropyrimidine in various solvents using HF/6-31++G(d,p) method





**FIG9: HOMO LUMO Images of 2,4-dihydroxy-5-fluoropyrimidine in various solvents using DFT/6-31++(d,p) method**



**FIG10: Mulliken charges graph of 2,4-dihydroxy-5-nitropyrimidine using HF/6-31++(d,p) and DFT/6-31++G(d,p)**

### III. Conclusion

The electronic absorption spectrum was calculated using TD-DFT method in various solvents and it was correlated with the experimental data. The homo lumo analysis has been made which indicate the eventual charge transfer interaction within the molecule. The hypsochromic shift was found due to the hydrogen bonding of the said compound by the solvent. The mulliken charges has discussed.

### Acknowledgement

B.S Yadav and Richa Sharma are thankful to UGC major project for the financial support.

### References

- [1]. Helmut Martin Hugel, Neale Jackson, Applied Sciences, 2, (2012), 558-565.
- [2]. F.M. Nejad and H.D. Stidham, Spectrochim Acta, 31A, (1975), 1433.
- [3]. R.K. Goel, N.K. Sanyal and S.L. Srivastava, Indian Journal of Pure and Applied Physics., 14, (1976), 842.
- [4]. Sakai K, Umemoto N, Aburai K, Takamastu Y, J.Oleo. Sci., 63(3),(2014), 257-267
- [5]. Blake D. Key, Robert D. Howell, Craig S. Criddle, American Chemical Society,31(9),(1997).
- [6]. I.L.Finar, Organic Chemistry, (Longman, Harlow), 2(19), (1975).
- [7]. R.S.Becker, A.B.F.Duncan, F.A.Matsen, Chemical Applications of Spectroscopy, Wiley, New York, 326, (1968).
- [8]. Bissantz C, Kuhn B, Stahi M, J. Med. Chem.,53(14), (2010), 5061-5084.
- [9]. S.N.Sharma, Ph.D. Thesis, Gorakhpur University, Gorakhpur, India (1975).
- [10]. Finar I L., Organic Chemistry, 2, (English Language Book Society, UK,(1975).
- [11]. D. Marjit, S.B. Benerjee, IJPAP, 11, (1973), 232.
- [12]. Mihaela Homocianu, Anton Airinei, Dana Ortansa Dorohoi, J. of Advanced Research in Physics, 2(1), (2011).
- [13]. S.F. Mason, J. Phillip and B K. Smith, J. Chem. Phys. 10, (USA) (1942), 428
- [14]. R.C. Lord and G.J. Thomas, Jr. Spectrochim Acta, 23A, (1967), 2551
- [15]. C.W.N. Cumper and A. Singleton, J. Chem. Soc., B, (1968), 649.
- [16]. Huffman BA, Poltash ML, Hughey CA, Anal Chem (Pubmed), 84(22), (2012), 42-50.
- [17]. Emilio Lizarraga, Diego M.Gil, Gustavo A. Echeverria, Oscar E. Piro, Cesar A.N. Cetelan, Aida Ben Altabef, Spectrochim Acta Part A, 127, (2014), 74-84.
- [18]. Hassan Moghanian, Akbar Mobionikhaledi, Roya Monjezi, Journal of Mol. Structure, 1052 (2013),135-145
- [19]. M.V.S. Prasad, N.Udaya Sri, A. Veeriah, J. At. Mol. Sci, 4(1), (2013), 1-17.
- [20]. K. Chaitanya, C. Santhamma, J.At. Mol. Sci., 3(1), (2012),1-22.
- [21]. Gnanasambandan, T., Gunasekaran, S. and Seshadri, S., International Journal of Recent Scientific Research, 3(7), (2012), 590-597
- [22]. Moamen S.Refat, International J. of Electrochem. Sci., 8, (2013).
- [23]. Mulliken, Robert S., Physical Review, 41(1),(1932), 41-49.
- [24]. Henryk Chojnacki, Int J. Mol. Sci, 4,(2003), 481-485.
- [25]. Ramon Carbo-Dorca, J. of Mathematical Chem., 36(3),(2004).