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STRUCTURAL, ELECTRONIC AND NONLINEAR OPTICAL PROPERTIES OF FLUOROPHENOL AND NITROPHENOL MOLECULES IN EFFECT OF ORTHO, PARA AND META POSITION

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In this present work, the theoretical studies on molecular structure of ortho (o), para (p) and meta (m) fluorophenol and nitrophenol, vibration spectra and non linear optical properties has been analysed by using B3LYP/6-31G basic set. The obtained minimum energy shows the stability of the molecule by comparative study. Based on the energy optimisation of the molecule the position of the nitrogen in the phenol ring is optimised at ortho state and fluorophenol is optimised at Meta state. Bond length, bond angle, energy gap, electron affinity, ionization potential, global hardness, softness, electronegativity, chemical potential, global electrophilicity index, vibrational spectra analysis based on FT-IR and FT-Raman frequency spectrum are investigated.

Keywords: Gaussian, FT-IR, FT-Raman, HOMO, LUMO, electrophilicity index

1. Introduction

In recently the researchers are interested to investigate about nonlinear optical (NLO) properties of organic materials. These organic materials are used for photonic application. Most of the photonic applications were occurring in the range of visible region and near-infrared light. The present work has been deal with effect of ortho, para and meta position of both fluorophenol and nitrophenol molecules in order to look into their structural, vibrational and nonlinear optical properties from IR spectrum, Raman spectrum and highest occupied molecular orbital (HOMO) and lowest un-occupied molecular orbital (LUMO) energy gap. Natural population and Mullikan population analysis has been evaluated on their charge distribution [1]. In current work Density Functional Theory (DFT) [2] has been implemented by using Gaussian 09 software. This software is useful to perform molecular electronic structure calculations in a rapid manner as opposed to using Slater type orbitals and it has improved performance by using Hartree–Fock calculations [3].

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The Hartree–Fock method is also called the self-consistent field method (SCF). It gives an approximate solution of the Schrödinger equation, thus, self-consistency was a requirement of the solution. Its solutions are behave as if each particle is subjected to the mean field created by all other particles and hence the terminology sustained, by means of an iterative method [4]. Gaussian software utilizes fundamental laws of quantum mechanics to predict energies, molecular structures, spectroscopic data (NMR, IR, UV, etc) and much more advanced calculations. The development of computational physics and chemistry provides an immense insight into electronic structures of molecules and strongly propels the development of the traditional experiments [5].

The FT-IR and FT-Raman spectrum for ortho, para and meta position of both fluoro and nitro derivatives of phenol were recorded and analysis are presented in our manuscript. In ortho, para and meta positions of fluorophenol, the structural changes of the ring are directed predominantly by the electro negativity of fluorine and the electrostatic potential around the molecule has been analysed through electron charge density [6]. Vibrational spectroscopy is used to analyse the structural features of present molecules and reasonable NLO properties. Their nonlinear optical response might consequence of electronic and non electronic process. Electronic nonlinearities arise as the result of the nonlinear response of bound electrons on an applied optical field [7]. In the organic material the nonlinear response is faster and reduce optical damage property than inorganic material and have high second harmonic generation efficiency [8] They have many applications in photoluminescence materials, optical materials and devices, organic light emitting diodes, photovoltaic cells and polarizing films [9].

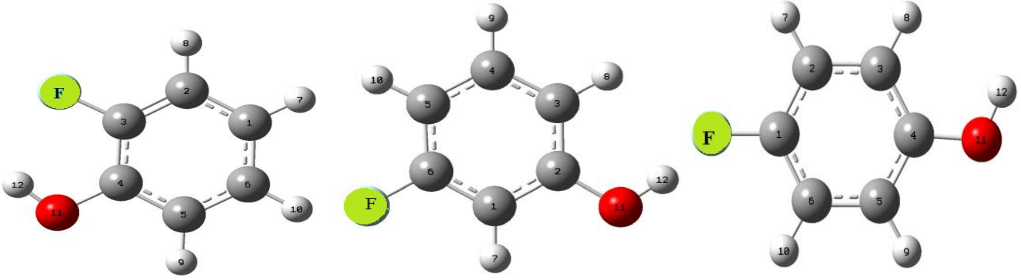
2. Methodology

The molecular structures of all the presented compounds were designed with the help of Gauss View 5.0.8 visualization program [10]. The ground state geometries are optimized by using Gaussian program. The optimized molecular structures are provided. The optimized structural parameters were used for the electron density calculation by Mulliken population analysis and vibrational frequency calculations at DFT level to characterize all the stationary points as minima. Becke's three-parameter hybrid functional combined with the correlation functional of Lee, Yang, and Parr (B3LYP) [11] which is one of the energy functional appeals single point energy calculation with 6-311G (d,p) [12,13] basis set used to describe electronic wave functions. Frequency calculations were performed at the same level of theory to confirm that the optimized geometry corresponds to the minimum energy in the potential energy surface with a high degree of accuracy by using Gauss view program. The charge transfer within the molecule is analysis from highest occupied molecular orbital (HOMO) to lowest unoccupied molecular orbital (LUMO). The optimized geometry structures with bond angle and bond length are provided with vibrational analysis.

3. Results and Discussion

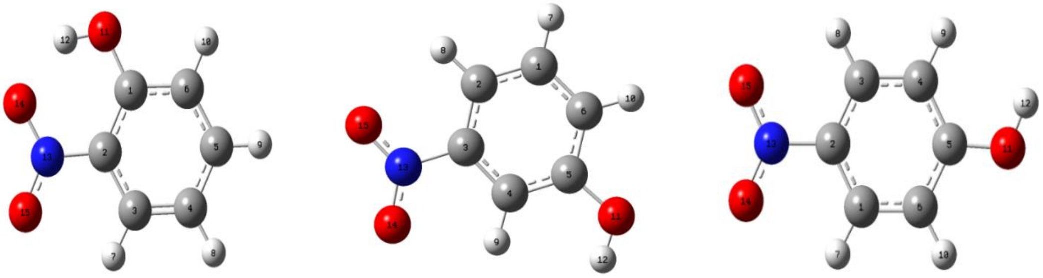
3.1 Geometry parameters

The optimized geometry parameters were taken for fluorophenol and nitrophenol in ortho, para and meta position and the results are analysed. The geometry optimization is a procedure to bring the molecule from higher energy (excited state) to lower energy (stabled state). The position of the fluorine/nitrogen changes in the phenol ring, based on the optimised energy of the molecule. The optimised energy of the o-fluorophenol, m-fluorophenol, p-fluorophenol is - 406.60104896 a.u., -406.60131757 a.u., -406.59998384 a.u. respectively. It shows that m-fluorophenol has a minimum/optimised energy when compare with the o-fluorophenol and p-fluorophenol. The optimised energy of the o-nitrophenol, m-nitrophenol, p-nitrophenol is -511.81739882 a.u., -511.80771070 a.u., -511.81000319 a.u. respectively. Hence o-Nitrophenol has been stabilized than other two states. The optimised structures of fluorophenol and nitrophenol are shown in Fig. 1a and 1b respectively.



o-fluorophenol m-fluorophenol p-fluorophenol

Fig. 1a. Optimized structure of fluorophenols



o-nitrophenol m-nitrophenol p-nitrophenol

Fig.1b: Optimized structure of nitrophenols

The Natural Bond Orbital (NBO) analysis is used to investigate the intra and intermolecular bonding and intermolecular interaction among bonds and charge transfer of the materials under study [14]. It is one of the efficient methods to study about intra and inter molecular bonding and charge transfer. It is also used to understand various second order interactions between the filled orbital and vacant orbital of sub systems. It gives information about interactions in both filled and virtual orbital spaces, which could enhance the analysis of intra and intermolecular inter actions [15]. The optimized bond length, bond angle and dihedral angle of the meta (m)-fluorophenol and (o)-nitrophenol are given in Table 1a and 1b respectively.

Table 1a

Bond length (Å), Bond Angle (°) and Dihedral Angle (°) of m-fluorophenol

S.No	Index of the atom	Bond Length (Å)	Index of the atom	Bond Angle (°)	Index of the atom	Dihedral Angle (°)
1.	1-2	1.39	2-1-6	117.90	6-1-2-3	0.00
2.	1-6	1.38	2-1-7	120.56	6-1-2-11	-180.00
3.	1-7	1.08	6-1-7	121.53	7-1-2-3	180.00
4.	2-3	1.40	1-2-3	120.74	7-1-2-11	0.00
5.	2-11	1.38	1-2-11	116.36	2-1-6-5	0.00
6.	3-4	1.39	3-2-11	122.89	2-1-6-13	-180
7.	3-8	1.08	2-3-4	119.46	7-1-6-5	180
8.	4-5	1.39	2-3-8	120.30	7-1-6-13	0.00
9.	4-9	1.08	4-3-8	120.23	1-2-3-4	0.00
10.	5-6	1.39	3-4-5	120.90	1-2-3-8	-180.00
11.	5-10	1.08	3-4-9	119.49	11-2-3-4	180.00
12.	6-13	1.39	5-4-9	119.60	11-2-3-8	0.00
13.	11-12	0.97	4-5-6	117.17	1-2-11-12	180.00
14.			4-5-10	122.10	2-3-11-12	0.00
15.			6-5-10	120.17	2-3-4-5	0.00
16.			1-6-5	123.26	2-3-4-9	180.00
17.			1-6-13	118.17	8-3-4-5	180.00
18.			5-6-13	118.55	8-3-4-9	0.00
19.			2-11-12	111.87	3-4-5-6	0.00
20.					3-4-5-10	180.00
21.					9-4-5-6	180.00
22.					9-5-4-10	0.00
23.					4-5-6-1	0.00
24.					4-5-6-13	180.00
25.					10-5-6-1	180.00
26.					10-5-6-13	0.00

Table 1b

Bond length (Å), Bond Angle (°) and Dihedral Angle (°) of o-nitrophenol

S.no.	Index of the atom	Bond Length (Å)	Index of the atom	Bond Angle(°)	Index of the atom	Dihedral Angle (°)
1.	C1-C2	1.4187	C1-C2-C6	118.19	6-1-2-3	0.01
2.	C1-C6	1.4063	C2-C1-O11	124.40	6-1-2-13	-179.98

3.	C1-O11	1.361	C6-C1-O11	117.40	11-1-2-3	180.01
4.	C2-C3	1.4077	C1-C2-C3	120.93	11-1-2-13	0.01
5.	C2-N13	1.4403	C1-C2-N13	120.83	2-1-6-5	-0.00
6.	C3-C4	1.3855	C2-C3-N13	118.23	2-1-6-10	179.99
7.	C3-H7	1.0821	C2-C3-C4	119.88	11-1-6-5	-180.00
8.	C4-C5	1.4109	C2-C3-H7	118.24	11-1-6-10	-0.01
9.	C4-H8	1.0834	C4-C3-H7	121.86	2-1-11-12	0.00
10.	C5-C6	1.3884	C3-C4-C5	119.55	6-1-11-12	180.00
11.	C5-H9	1.0848	C3-C4-H8	120.07	1-2-3-4	-0.01
12.	C6-H10	1.0828	C5-C4-H8	120.36	1-2-3-7	-180.00
13.	O11-H12	0.9953	C4-C5-C6	120.87	13-2-3-4	179.98
14.	N13-O14	1.29	C4-C5-H9	119.73	13-2-3-7	-0.00
15.	N13-O15	1.2594	C6-C5-H9	119.39	1-2-13-14	-0.02
16.			C1-C6-C5	120.55	1-2-13-15	179.97
17.			C1-C6-H10	117.43	3-2-13-14	-180.02
18.			C5-C6-H10	122.01	3-2-13-15	-0.02
19.			C1-O11-H12	109.36	2-3-4-5	0.00
20.			C2-N13-O14	118.48	2-3-4-8	180.00
21.			C2-N13-O15	119.68	7-3-4-5	179.99
22.			O14-N13-O15	121.82	7-3-4-8	-0.00
23.					3-4-5-6	0.00
24.					3-4-5-9	-179.99
25.					8-4-5-6	-179.99
26.					8-4-5-9	0.00
27.					4-5-6-1	-0.00
28.					4-5-6-10	-180.80

3.2 HOMO-LUMO Energy

The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are also called as frontier orbital [16]. The energy difference between the HOMO-LUMO shows the stability of the structure. In the present work HOMO and LUMO energy is calculated by B3LYP/6-31G* method. LUMO is the unoccupied molecular orbital of the acceptor molecule and HOMO is the highest occupied molecular orbital of the donor molecule. The highest occupied molecular orbital has occupied more electrons where lowest unoccupied molecular orbital has minimum number of electrons. The difference between the HOMO-LUMO is estimated as HOMO-LUMO energy gap (Eg). The E_{HOMO} and E_{LUMO} is used to approximate the ionization potential (I) and electron affinity (A) given by Koopmans' theorem [17], respectively.

In the present work, the Fluorine/Nitrogen atom has been placed in the ortho, meta and para position of the phenol ring and the E_{HOMO} and E_{LUMO} has been calculated. This calculation and obtained Eg confirms the stability of Meta – fluorophenol and ortho- nitrophenol, shown in Fig.2a and 2b respectively.

Fig. 2a. HOMO and LUMO of m-fluorophenol

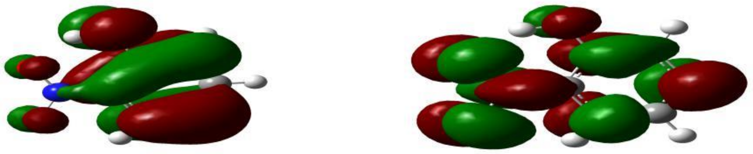


Fig. 2b. HOMO and LUMO of o-nitrophenol

The HOMO-LUMO energy gap (Eg) of meta – fluorophenol and ortho-nitrophenol are -0.2258 eV and -0.1392 eV respectively. According to Koopman's theorem, ionization potential (I) and electron affinity (A) are related to,

$$I = -E_{\text{HOMO}} \text{ ----- } (3.1)$$

$$A = -E_{\text{LUMO}} \text{ ----- } (3.2)$$

The chemical potential (Pi), electronegativity (χ) and hardness (η) can be estimated with,

$$Pi = -[I + A]/2 \text{ ----- } (3.3)$$

$$\chi = [I + A]/2 \text{ ----- } (3.4)$$

$$\eta = [I - A]/2 \text{ ----- } (3.5)$$

Global electrophilicity index (ω) is defined as

$$\omega = Pi^2 / 2\eta \text{ ----- } (3.6)$$

Global softness (σ) is given by [18],

$$\sigma = 1/\eta \text{ ----- } (3.7)$$

all the calculated values are given in Table 2.

Table 2

Reactivity descriptors of o-nitrophenol and m- fluorophenol

Parameters (in a.u)	ortho - nitrophenol	meta -fluorophenol
Ionisation Potential (I)	0.2581	0.2364
Electron Affinity (A)	0.1189	0.0106
chemical potential (Pi)	-0.1885	-0.1235
Electro negativity (χ)	0.1885	0.1235
hardness (η)	0.0696	0.1129
Electrophilicity index (ω)	0.2553	0.0675
softness (σ)	14.3678	8.8574

From comparative analysis ortho nitrophenol has high chemical reactivity due to its high global softness value than meta fluorophenol. Hence the atoms in nitrophenol molecules are ready to share the electrons to create the covalent bond.

The low Electrophilicity index (0.0675 a.u) of fluorophenol represents its less toxicity. These factors can help in molecular design problems relevant to absorption, i.e. in layered photovoltaic materials.

3.3. Non-linear optical Properties

Non-linear optical NLO behaviors of the studied molecules were investigated by determining the electric dipole moment μ, the polarizability α by using the same methods [19]. The computed dipole moment and polarisability of ortho-nitrophenol and meta-fluorophenol are 4.2781 (D); 24.0827 (esu) and 3.3733 (D); 20.350 (esu) respectively. The intermolecular interactions involving the non-bonded type dipole–dipole interactions, in a molecule is explicitly known by the dipole moment. The higher dipole moment leads to the stronger the intermolecular interactions [20]. In the present study the reported dipole moment shows that the interactions in both the molecules of under study are high. Even it is very high in ortho - nitrophenol than meta - fluorophenol. The other factor namely polarizability is also used to determine the intermolecular force. In this study the polarizability of reported molecules is high and depicts the stronger intermolecular force it creates. It is evidently proved by its dipole moment too. Polarizability is usually refers to the tendency of matter and it is also responsible for dielectric constant and, at high (optical) frequencies, its refractive index. The rotational constants (GHz) of ortho – nitrophenol and m-fluorophenol along x,y and z axes are 2.32504, 1.26294, 0.81840; 3.69035, 1.76094, 1.19210 respectively. The force should be less over the molecules to obtain the stabled state. Here, The Cartesian Forces (Hartrees/Bohr) acting on the materials is 0.02932, 0.000028961 for o – nitrophenol and m – fluorophenol respectively. The Angle between quadratic step and forces is 62.23 degrees (o – nitrophenol) and 30.41 degrees (m – fluorophenol). Electronic spatial extent $<R^2>$ in au is 1319.2394 (o – nitrophenol) and 910.3591 (m-fluorophenol), which is used to analyze its molecular volume. The thermal energy, constant volume molar heat capacity (CV), Entropy (S), Zero-point vibrational energy are 72.443 KCal/Mol, 64.779 KCal/Mol; 29 Cal/Mol-Kelvin, 24.579 Cal/Mol-Kelvin; 86 Cal/Mol-Kelvin, 78.892 Cal/Mol-Kelvin; 283530.7 (Joules/Mol), 254623.4 (Joules/Mol) respectively. The diagonal vibrational polarizability and diagonal vibrational hyperpolarizability of ortho – nitrophenol and m-fluorophenol along x,y and z axes are 10.4236749, 12.5077743, 15.9431981 ; 10.4680880, 3.6742536, 38.8448859 and 178.9096859, 1.4460139, 0.1486463; 24.0276905, 8.2629922, -0.0055482 respectively. The hyperpolarizability furnishes the information regarding the material capability to generate second order non-linear effects and regulates the ensuing experiments [7]. The hyperpolarizability and intra molecular interactions are the important criteria to elucidate the nonlinear optical properties, which are discussed in the present study. Therefore, a theoretical correlation between molecular structure and NLO properties may suggest the possibilities of design and synthesis of new NLO materials [21]. All the calculated factors are target of an optimization in materials design, to prove its nonlinear properties. Out of the proposed material ortho – nitrophenol is expected as a good nonlinear material than meta-fluorophenol.

3.4 Vibrational spectra analysis

The FT-IR and FT-Raman frequency spectrum are analysed with their vibrations of both fluoro and nitro derivatives of phenol in their ortho, para and meta positions.

C-H Vibrations

In fluorophenol, the C-H stretching vibration **occurs above 3000 cm^{-1} [19]. The modes (29,30,31,32,33) at the range from** 3194 cm^{-1} to 3672 cm^{-1} were recorded. C-H out-of-plane bending vibrations appear in the range of 1000-750 cm^{-1}. The normal mode (10,12,13,14) at the range from 711 cm^{-1} to 889 cm^{-1} were observed a C-H out-of-plane vibration. The range of 983 cm^{-1}-1213 cm^{-1} observed the bending of the C-H molecule vibrations with the maximum FT-Raman frequency at 1031cm^{-1}.

In nitrophenol at C-H vibrations, the IR intensity is falls from 1.16 to 9 Km/mol (7 Km/mol [22]), FT-IR frequency is in the range from 3200 cm^{-1} to 3270 cm^{-1} (around 3000 [22]).

C-C Vibrations

In fluorophenol, the C-C stretching frequency is recorded at the range from 1539 cm^{-1} to 1678 cm^{-1} [23] and 1411 cm^{-}1. The FT-Raman frequency at 1678 cm^{-1} C-C stretching vibration is high in the o-fluorophenol.

In nitrophenol, the maximum IR intensity at C-C vibration is falls over p-nitrophenol and it is agreed well with available literature [22].

O-H Vibrations

In fluorophenol, the O-H molecule the out-of-plane bending occurs below 300 cm^{-1} region [24]. The bending vibration occurs in the region 346 cm^{-1}. FT-Raman maximum intensity of the bending vibration of the O-H group is at 346 cm^{-1} in para position.

C-F Vibrations

C-F molecule vibration has a symmetry deformation vibration range from 247 cm^{-1} to 333 cm^{-1}. The calculated FT-IR frequency is minimum for meta fluorophenol and maximum at para fluorophenol. FT-Raman intensity is maximum at meta fluorophenol.

6. Conclusions

In this work the ab initio study is made on fluorophenol and nitrophenol in ortho, para and meta states and it is concluded that fluorophenol is more stable at meta state and nitrophenol is more stable at ortho state. FT-IR spectrum of the m-fluorophenol has low intensity peak than other positions whereas in the FT-Raman spectrum of m-fluorophenol has a greater number of peaks due to the C-H stretching vibration. FT-IR spectrum of the o-nitrophenol has more number of vibration peaks than the other positions. By using HOMO and LUMO analysis the energy parameters, chemical potential, electronegativity, hardness, Global electrophilicity index, Global softness are computed and the conclusions are nitrophenol molecules are ready to share its valence electrons to create the covalent bond; fluorophenol has less toxicity due to its low Electrophilicity index (0.0675 a.u). The reported dipole moment (> 3) shows the intermolecular interactions in both the molecules of under study are high. The computed polarisability of the proposed materials represents, o-nitro phenol has high refractive index than m-fluorophenol and predicted as good nonlinear material.

REFERENCES

[1]. *Tian Shia, Ping Wang,* "GPView: A Program for Wave Function Analysis and Visualization" in Chemical Physics, **vol. 1**, no.3, Jan. 2020, pp. 01-39.

[2]. *D.S. Jayalakshmi, M.Sundareswari, E.Viswanathan,* "Theoretical Prediction of Possible Coexistence Of Superconductivity And Antiferromagnetism In Novel SrFeRubi$_2$, SrRu$_2$Bi$_2$ and Parent SrFe$_2$Bi$_2$ Compounds" Scientific Bulletin : Series A, **vol. 8,** no.2, Feb. 2019, pp.221-232.[3]. M.J. Frisch et al., Gaussian 09, Revision A.02. Gaussian, Inc., Wallingford, Nov. 2016.

[4]. *Hinchliffe, Alan*, Modelling Molecular Structures (2nd ed.). Baffins Lane, Chichester, West Sussex PO19 1UD, England: John Wiley & Sons Ltd.,2000.

[5] *Amel Bendjeddou, Tahar Abbaza,B, Abdelkrim Gouasmiab And Didier Villemin,"*Quantum Chemical Studies On Molecular Structure And Reactivity Descriptors Of Some P-Nitrophenyl Tetrathiafulvalenes By Density Functional Theory (Dft)" Acta Chim. Pharm. Indica, **vol. 6,** no.2, 2016, pp. 32-44.

[6]. *Wiktor Zierkiewicz et al., "*σ-Aromaticity and σ-Antiaromaticity in Alkali Metal and Alkaline Earth Metal Small Clusters", J. Phys. Chem. A, **vol. 107,** no.4, Jan. 2003, pp.554-560.

[7]. *Aslı Esme and Seda Gunesdogdu sagding*, "The linear, nonlinear optical properties and quantum chemical parameters of some sudan dyes" *BAU Fen Bil. Enst. Dergisi Cilt* **vol. 16**, no.1,2014, 47-75.

[8]. *M.Victor Antony Raj, J. Madhavan,M.Gulam Mohamed*, "Structural and Density Functional Theory Investigation on L-Alaninium Maleate (LAM) single crystal an organic NLO Material" J.Comput. Method Mol. Design, **vol.1,** no.4, 2011, pp. 57-64

[9]. *S. Siyamak et al.,* "Molecular structure and UV–Vis spectral analysis of new synthesized azo dyes for application in polarizing films"Dyes Pigm, **vol. 129**, June 2016, pp.9–17.

[10]. *R. Dennington et al.*, Gaussview, version 5 Semichem Inc., Shawnee Mission, KS, 2009 [11]. *A.D. Becke*, "Density-functional thermochemistry. III. The role of exact exchange"J Chem Phys, **vol. 98**, 1993,pp. 5648–52.

[12]. *G.A. Petersson et al.*, "A complete basis set model chemistry. I. The total energies of closed-shell atoms and hydrides of the first-row elements " J Chem Phys., **vol. 89**, Aug.1988, pp.2193.

[13]. *G.A. Petersson, M.A. Al-Laham,* "A complete basis set model chemistry. II. Open-shell systems and the total energies of the first-row atoms" J Chem Phys., **vol. 94**, Aug. 1991, pp.6081–6090

[14]. *Hacer Pir Gumus et al*., " Theoretical investigations on nonlinear optical and spectroscopic properties of 6 – (3,3,4,4,4-penta fluora -2-hydroxls-1-butenyl)-2,4-pyrimidinedione: An efficient NLO materials" Russian Journal of Physical Chemistry A, **vol. 88**, no.13 ,2014, pp.2348-2358.

[15]. *F.Weinhold and C.R.Landis,* Valency and Bonding, Cambridge Univ. Press, 2005.

[16]. *V.Mohankumar, P.Pounraj, M.Senthil Pandian, P.Ramasamy,* "effect of flavones and iso flavones in the triphenylamine based sentisizers for dye sentisized solar cell application: DFT and TD-DFT approach", Silicon, **vol.11**, 2019, pp.1205-1220.

[17]. *T.C. Koopmans,* "Über die Zuordnung von Wellenfunktionen und Eigenwerten zu den Einzelnen Elektronen Eines Atoms" Physica (Amsterdam), **vol. 1**, 1933, pp. 104-113.

[18]. *Ebenso, E.E., Arslan, T., Kandemirli, F., et al.,* "Theoretical studies of some sulphonamides as corrosion inhibitors for mild steel in acidic medium" International Journal of Quantum Chemistry, **vol. 110**, no. 14, 2010, pp. 2614-2636,

[19]. *M. Suhasini, E. Sailatha, S. Gunasekaran, G.R. Ramkumaar* "Vibrational and electronic investigations, thermodynamic parameters, HOMO and LUMO analysis on Lornoxicam by density functional theory", J. Mol. Struc., **vol.1100**, Nov. 2015, pp.116-128.

[20]. *G. Varsanyi*, Wiley, Assignments of Vibrational Spectra of 700 Benzene Derivatives, New York, 1974.

[21]. *Anuj Kumar And Mahesh Pal Singh Yadav, "*Computational studies of third-order nonlinear optical properties of pyridine derivative 2-aminopyridinium p-toluenesulphonate crystal" Pramana – J. Phys. **vol. 89,** no. 7, 2017, pp.1-7.

[22]. *Agnieszka J. Gordon (Abkowicz-Bienko) Zdzisław Latajka Dariusz C Bienko,* "Theoretical infrared spectrum and revised assignment for para-nitrophenol. Density functional theory studies" Chemical Physics, **vol. 250**, no.2, Dec. 1999, pp.123-129

[23] *G. Varsanyi,Wiley,* Assignments of Vibrational Spectra of 700 Benzene Derivatives, New York, 1974.

[24]. *D.N. Sathyanarayana,* Vibrational Spectroscopy Theory and Applications, second ed., New Age International (P) Limited Publishers, New Delhi, 2004.