

# THEORETICAL INVESTIGATION OF ELECTROSTATIC POTENTIAL AND NON LINEAR OPTICAL PROPERTIES OF M-NITROACETANILIDE

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## ABSTRACT

In this paper, we report the electrostatic potential and nonlinear optical properties of meta-nitroacetanilide. Molecular properties were calculated by Hartree Fock (HF) and density functional theory (DFT) methods with the 6-31+G (d) basis set. The molecular electrostatic potential map indicates that the negative potential sites are on oxygen atoms as well as the positive potential sites are around the hydrogen atoms. The second-order nonlinear optical properties based on the first static hyperpolarizability ( $\beta$ ) have been investigated. The calculated results show that the title molecule might have nonlinear optical behavior. The thermodynamic functions (entropy, heat capacity and enthalpy) were obtained from spectroscopic data by statistical methods for the range of temperature 100–1000 K.

**Keywords:** Organic compound, dipole-moment, first hyperpolarizability, HOMO-LUMO, Nonlinear optical materials.

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## INTRODUCTION

Nitroacetanilide, commonly known as NAa, an organic nonlinear optical (NLO) compound with formula  $C_8H_8N_2O_3$ . Nitroacetanilide is an organic molecule containing extended  $\pi$ -conjugated electrons and characterized by large values of molecular first hyperpolarizabilities showing enhanced NLO properties. As known, the origin of non-linearity in organic molecules is significantly related to the presence of delocalized  $\pi$ -electron system linking donor and acceptor groups, which amplify the obligatory asymmetric polarizability.<sup>1</sup> The NLO properties magnitude of molecules is dependent on the first-order hyperpolarizability. The NLO property of molecules and their hyperpolarizabilities have become an important field of extensive research.<sup>2-6</sup>

Several authors already reported synthesis, molecular structure and vibrational spectroscopic investigations of nitroacetanilide.<sup>7-9</sup> More recently, the molecular structure; vibrational spectroscopic and Natural Bond Orbital (NBO) studies of meta-NAa have been investigated by Li Xiao-Hong et al.<sup>10</sup>

In the present work, we are interested to the Meta form of nitroacetanilide molecule (m-NAa). We report here for the first time in literature the electrostatic potential and the nonlinear optical properties of m-NAa. To our knowledge, the NLO properties have not been reported except in our work. The HOMO and LUMO analyses have been used to elucidate information regarding charge transfer within the molecule. Finally, the thermodynamic properties of the optimized structure were obtained theoretically from the harmonic vibrations taken from.<sup>10</sup>

## EXPERIMENTAL

The first task for the computational work was to determine the optimized geometry of the molecule. The molecular structure of m-NAa is optimized by Hartree-Fock (HF) level and density functional theory (DFT) using 6-31+G(d) basis set, by the Berny method.<sup>11-13</sup> In the DFT method, The effects of electron correlation on the geometry optimization are taken into account by Becke's three parameter hybrid exchange functions and Lee-Young-Parr correlation functional (B3LYP) level.<sup>14,15</sup> The optimized structure was then used to calculate the electrostatic potential and nonlinear optical properties of m-NAa

molecule. The 6-31+G (d) basis set for both HF and DFT levels has been found to be more adequate for obtaining reliable trends in hyperpolarizability ( $\beta$ ) values.<sup>16,17</sup> All theoretical calculations were performed using Gaussian 09 program and Gauss-View molecular visualization program package on the personal computer.<sup>18,19</sup> The optimized geometry of m-nitroacetanilide which was performed by HF and B3LYP methods is shown in Fig.-1. The obtained structure was used to calculate the different properties of the title molecule.

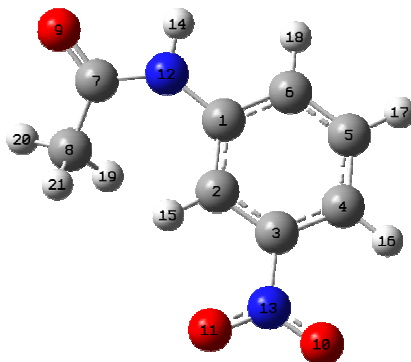


Fig.-1: Optimized geometry of M-Nitroacetanilide.

## RESULTS AND DISCUSSION

### Molecular electrostatic potential

Molecular Electrostatic Potential (MEP) generally presents in the space around the molecule by the charge distribution. The MEP is related to the electronic density and is a very useful descriptor for determining sites for electrophilic attack and nucleophilic reactions as well as hydrogen-bonding interactions.<sup>20-24</sup> The electrostatic potential  $V(r)$  are also well suited for analyzing processes based on the “recognition” of one molecule by another, as in drug receptor, and enzyme substrate interactions, because it is through their potentials that the two species first “see” each other.<sup>25-26</sup> Being a real physical property  $V(r)$  can be determined experimentally by X-ray diffraction or by computational methods.<sup>27</sup>

The electrostatic potential  $V(r)$ , at a given point  $r(x, y, z)$  in the space around a molecule (in atomic units) is defined in terms of the interaction energy between the electrical charge generated from the molecule electrons and nuclei and positive test charge (a proton) located at  $r$  and can be expressed as:

$$V(\vec{r}) = \sum_A \frac{Z_A}{|R_A - \vec{r}|} - \int \frac{\rho(\vec{r}') d\vec{r}'}{|\vec{r}' - \vec{r}|}$$

Where  $Z_A$  is the charge on nucleus A, located at  $R_A$  and  $\rho(r)$  is the electronic density function for the molecule. The first and second terms represent the contributions to the potential due to nuclei and electrons, respectively.  $V(r)$  is the resultant electrical potential at each point  $r$ , which is the net electrostatic effect produced at the point  $r$  by both the electrons and nuclei of the molecule. The molecular electrostatic potential (MEP) serves as a useful quantity to explain hydrogen bonding, reactivity and structure-activity relationship of the molecules.<sup>28</sup>

In order to predict the molecular reactive sites, the MEP for the title molecule was calculated using 6-31+G (d) basis set as shown in Fig.-2. The different values of the electrostatic potential at the surface are represented by different colors, where blue indicates the highest electrostatic potential energy and red indicates the lowest electrostatic potential energy. As it can be seen from the MEP map of m-NAa molecule, the region around oxygen atoms linked with carbon through double bond represents the most negative potential region (red). The most negative  $V(r)$  value is associated also with  $\text{NO}_2$  group of m-NAa. The hydrogen atoms attached to nitrogen atoms possess the maximum positive charge. The MEP surface provides necessary details about the reactive sites.

### Nonlinear optical properties

Theoretical investigations have been done in order to understand the microscopic origin of nonlinear behavior of the studied molecule. The study involves the calculation of dipole moment ( $\mu$ ), polarizability ( $\alpha$ ) and first hyperpolarizability ( $\beta$ ) tensor for the title molecule. First hyperpolarizability is a third rank tensor which can be described by a  $3 \times 3 \times 3$  matrix. Due to the Kleinman symmetry, the 27 components of the 3-D matrix can be reduced to 10 components.<sup>29</sup> The Gaussian 09 output provides 10 components of this matrix as  $\beta_{xxx}$ ,  $\beta_{xyy}$ ,  $\beta_{xyy}$ ,  $\beta_{yyy}$ ,  $\beta_{xxz}$ ,  $\beta_{xyz}$ ,  $\beta_{yyz}$ ,  $\beta_{xzz}$ ,  $\beta_{yzz}$ ,  $\beta_{zzz}$  respectively. Many types of hyperpolarizabilities have been reported in the literature denoted as  $\beta_{vec}$  ( $\beta$  vector),  $\beta_{||}$  ( $\beta$  parallel),  $\beta_{tot}$  ( $\beta$  total).<sup>30</sup>  $\beta_{vec}$  is the component along the dipole moment direction. But the theoretical chemists are concerned with  $\beta_{||}$  which is the component parallel to the ground state charge transfer direction and the other is the total hyperpolarizability  $\beta_{tot}$ .

Using the  $x$ ,  $y$  and  $z$  components, and the magnitude of the total static dipole moment ( $\mu$ ) and isotropic polarizability ( $\alpha$ ), first-order hyperpolarizability  $\beta_{tot}$  tensor can be calculated by the following equations:

$$\mu_0 = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2}$$

$$\alpha = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$$

$$\beta_{tot} = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2}$$

The complete equation for calculating the magnitude of the first hyperpolarizability ( $\beta$ ) from Gaussian 09 output is given below:

$$\beta_{tot} = \left[ (\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{yyy} + \beta_{yzz} + \beta_{yxx})^2 + (\beta_{zzz} + \beta_{zxx} + \beta_{zyy})^2 \right]^{1/2}$$

To calculate the hyperpolarizability, the origin of the Cartesian coordinate system was chosen as the centre of mass of the molecule.<sup>31</sup> Since the values of the first hyperpolarizability tensors are reported in atomic units (a.u.), the calculated values were converted into electrostatic units.

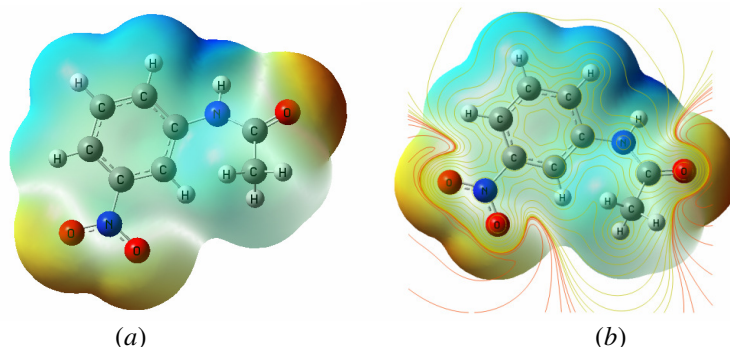


Fig.-2: Molecular electrostatic potential maps of m-nitroacetanilide, (a) 3D plot, (b) contour map.

The calculated dipole moment ( $\mu$ ), mean polarizability ( $\alpha$ ) and first hyperpolarizability ( $\beta$ ) of the title molecule have been computed at HF/6-31+G(d) and DFT-B3LYP/6-31+G(d) levels of theory to provide its nonlinear properties and are listed in Table-1. The dipole moment is a basic property of a molecule, used to investigate intermolecular interactions concerning the non-bonded type dipole-dipole interaction. Higher the dipole moment, stronger is the inter-molecular interaction. The small frontier orbital energy gap (between 3.91634 and 11.39337 eV by both methods) and high dipole moment (between 3.5642 and 5.7166 Debye) of m-NAA may contribute to multiply its NLO activity. Based on predicted dipole moment values in Table 1, it is found that, in going from the gas phase (4.5164 D and 3.5642 D obtained using HF

and DFT methods, respectively) to the solvent phase (5.7166 D and 4.7853 D in methanol obtained using HF and DFT levels of theory, respectively) the dipole moment value increases.

The highest value of dipole moment is observed for component  $\mu_y$ . In this direction, this value is equal to 4.4175 and 5.6244 Debye by HF level of theory in gas phase and solvent, respectively, and 3.4817 and 4.6961 Debye by DFT level of theory in gas phase and solvent. These values indicate the eventual charge transfer direction within the molecule.

Table-1: Calculated dipole moment ( $\mu$ ), polarizability ( $\alpha$ ) and hyperpolarizability ( $\beta_{\text{total}}$ ) in gas and solution of m-nitroacetanilide.

Parameters	Gas		Methanol	
	HF/6-31+G(d)	DFT/6-31+G(d)	HF/6-31+G(d)	DFT/6-31+G(d)
$\mu_x$	-0.0715	0.2797	-0.2008	0.1829
$\mu_y$	4.4175	3.4817	5.6244	4.6961
$\mu_z$	0.9371	0.7094	1.0024	0.9014
$\mu$ (D)	4.5164	3.5642	5.7166	4.7853
$\alpha_{xx}$	128.5129	156.3688	161.3246	204.3185
$\alpha_{xy}$	-4.9179	-6.3250	-4.9715	-5.5196
$\alpha_{yy}$	102.2669	121.28619	135.4042	164.0271
$\alpha_{yz}$	-9.9720	-5.9193	-14.7527	-9.8573
$\alpha_{yz}$	6.6021	3.3854	10.5792	6.5892
$\alpha_{zz}$	54.9548	47.7254	68.2885	59.8728
$\alpha$ (a.u)	95.2449	108.4601	121.6724	142.7395
$\alpha$ [ $10^{-23}$ esu]	14.1153	16.0738	18.0318	21.1540
$\beta_{xxx}$	-52.2768	-364.9886	-152.3107	-870.4614
$\beta_{xxy}$	-98.2989	-127.1696	-272.7764	-394.2242
$\beta_{xyy}$	-74.1206	-135.0980	-212.2388	-466.5415
$\beta_{yyy}$	53.6648	-66.7881	78.3273	-320.9485
$\beta_{xxz}$	51.4268	61.0933	89.3759	128.9908
$\beta_{xyz}$	-38.9825	-61.7524	-57.5877	-142.0379
$\beta_{yyz}$	36.4292	2.4031	80.5493	-9.1074
$\beta_{xzz}$	22.7114	-0.7770	46.5831	-2.7910
$\beta_{yzz}$	8.5259	-9.2885	12.0811	-15.5999
$\beta_{zzz}$	-5.5154	9.0943	-16.4644	16.8891
$\beta$ (a.u)	137.2390	545.3831	397.3801	1532.2477
$\beta$ [ $10^{-30}$ esu]	1.1856	4.7117	3.4331	13.2375

Polarizability and total hyperpolarizability of the title molecule are calculated to be (between  $14.1153 \times 10^{-23}$  and  $21.1540 \times 10^{-23}$ ) esu and ( $1.1856 \times 10^{-30}$  and  $13.2375 \times 10^{-30}$ ) esu, respectively (see Table 1).

For polarizability, DFT method gives higher values ( $16.0738 \times 10^{-23}$  and  $21.1540 \times 10^{-23}$  esu) compared to those calculated using HF method ( $14.1153 \times 10^{-23}$  and  $18.0318 \times 10^{-23}$  esu).

Accordingly to the results, polarizability values obtained in solvent phase ( $18.0318 \times 10^{-23}$  and  $21.1540 \times 10^{-23}$  esu) are most important compared to those obtained in gaseous phase ( $14.1153 \times 10^{-23}$  and  $16.0738 \times 10^{-23}$  esu). So, from the gas phase to the solvent phase, polarizability values increase.

The magnitude of the molecular hyperpolarizability  $\beta$ , is one of key factors in NLO system. The calculated first static hyperpolarisability  $\beta$  value is equal to  $1.1856 \times 10^{-30}$  and  $4.7117 \times 10^{-30}$  and calculated at HF and DFT levels of theory in gas phase, respectively. In solvent phase, these values are  $3.4331 \times 10^{-30}$  and  $13.2375 \times 10^{-30}$  and calculated at HF and DFT levels of theory, respectively. Accordingly to the results, DFT method gives interesting values of  $\beta$ .

The calculated first order hyperpolarizability of p-nitroacetanilide (PNA) is  $11.482 \times 10^{-30}$  esu as reported by T. Gnanasambandan et al.<sup>9</sup> This value is two times greater than the mean  $\beta$  value ( $5.6419 \times 10^{-30}$  esu)

of the title molecule. Urea is the reference molecule which is used in the study of the NLO properties of molecular systems. Therefore, it is used commonly as a threshold value for comparative purpose. Calculated  $\beta_{total}$  value for the title molecule ( $5.6419 \times 10^{-30}$  esu) is found to be 29 times greater than the  $\beta_{total}$  value of urea ( $0.1947 \times 10^{-30}$  esu), predicting that m-NAA is an efficacious candidate for NLO material.

### HOMO and LUMO analysis

Molecular orbitals and their properties such as energy are very useful for scientists and are very important parameters for quantum chemistry. The most important orbitals in a molecule which determine how the molecule interacts with other species are the frontier molecular orbitals, called highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). They are the key parameters in determining molecular properties and molecular electrical transport properties.<sup>32,33</sup> Moreover, the Eigen values of HOMO ( $\pi$  donor) and LUMO ( $\pi$  acceptor) and their energy gap reflect the chemical activity of the molecules.

We have done optimization in order to investigate the energetic behavior of m-NAA molecule in gas and solution. The total energy and frontier molecular orbital energies have been calculated with HF/6-31+G (d) and B3LYP/6-31+G (d) levels. Results obtained from solvent (methanol) and gas phase are listed in Table-2.

Table-2: Calculated Energies values in gas and solution of m-nitroacetanilide using 6-31+G (d) basis set.

Parameters	Gas		Methanol	
	HF	DFT	HF	DFT
Energy	-641.0017177	-644.7744698	-641.0186747	-644.7873947
$E_{Homo}$	-10.10797	-6.75243	-9.85465	-6.59135
$E_{Lumo}$	1.28540	-2.64508	1.39451	-2.67501
$E_{Homo-Lumo}$ gap (eV)	11.39337	4.10735	11.24916	3.91634
$E_{Homo-1}$	-10.53837	-7.305104	-10.17906	-7.26104
$E_{Lumo+1}$	2.705312	-1.054	3.094	-0.83477
$E_{Homo1-Lumo+1}$ gap (eV)	13.24368	6.25110	13.27306	6.42627

The energy gap values are 11.39337, 4.10735, 11.24916 and 3.91634 eV in gas and solution for m-nitroacetanilide molecule, respectively. The optical band gap calculated using B3LYP/6-31+G (d) was found to be 4.10 eV which is in accordance with the gap of other nonlinear optical materials.<sup>34,35</sup>

The molecular orbital (MO) calculation indicates that m-nitroacetanilide has 47 occupied MOs. We examine the four important molecular orbitals (MOs): the second highest and highest occupied MOs and the lowest and the second lowest unoccupied MOs which we denote HOMO-1, HOMO, LUMO and LUMO+1, respectively. These MOs for gas phase are represented in Fig.-3.

The energy gap between HOMO and LUMO indicates molecular chemical stability. In addition, a lower HOMO-LUMO energy gap (3.91634 eV) was obtained with DFT/6-31+G (d) using methanol solvent. This value explains the fact that eventual charge transfer interaction is taking place within the molecule. However, HOMO-LUMO energies are influenced not only by the basis set employed in HF and DFT calculations but also by the solvent in which the molecule is contained.

From the above results, it can be inferred that the DFT method estimated better the value of the band gap. The distributions of the HOMO-1, HOMO, LUMO and LUMO+1 orbitals computed at the DFT/6-31+G(d) method for the title molecule are shown in Fig.-3. As can be seen from Fig.-3, the HOMO and LUMO+1 are delocalized over the entire molecule. Whereas, the HOMO-1 is delocalized over the NHCOR-CH<sub>3</sub> moiety which acts as electro donor group, while the LUMO is delocalized over the nitrobenzene moiety. The nitro group acts as electro donor.

### Thermodynamic properties

On the basis of vibrational analysis at B3LYP/6-31+G(d,p) level as reported by Li Xiao-Hong et al., the standard statistical thermodynamic functions: entropy, heat capacity and enthalpy changes of m-NAA

molecule were obtained from the theoretical harmonic frequencies and are listed in Table-3. Thermodynamic parameters were obtained using both HF and DFT methods with 6-31+G (d) basis set. From Table-3, we can observe that these thermodynamic functions are increasing with temperature ranging from 100 to 1000 K due to the fact that the molecular vibrational intensities increase with temperature.<sup>36</sup>

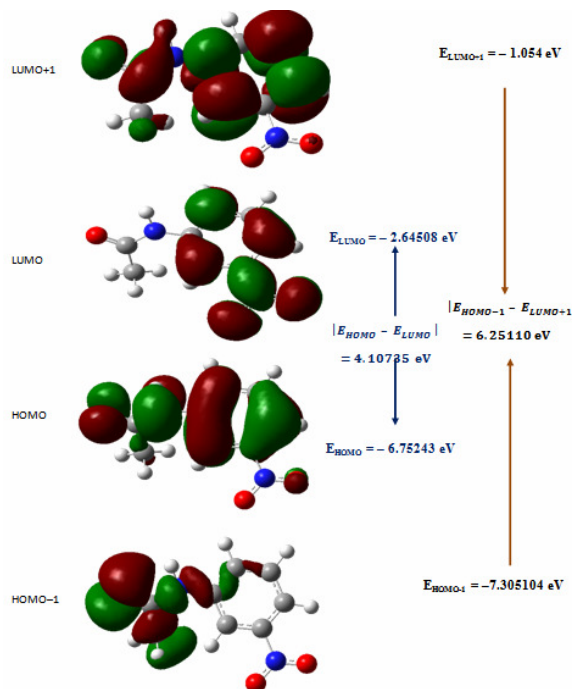


Fig.-3: Plots of the frontier orbitals of m-nitroacetanilide by B3LYP/6-31+G (d)

Table-3: Thermodynamic properties for meta-nitroacetanilide

T(K)	HF/6-31+G (d)			DFT/6-31+G (d)		
	S(J/mol.K)	Cp (J/mol.K)	ddH(kJ/mol)	S(J/mol.K)	Cp(J/mol.K)	ddH(kJ/mol)
100.00	316.83	86.37	6.01	334.62	90.60	6.55
200.00	392.63	139.34	17.25	412.96	142.56	18.15
293.15	455.15	190.74	32.63	476.64	193.63	33.82
298.15	458.40	193.43	33.59	479.94	196.31	34.79
300.00	459.60	194.42	33.95	481.16	197.30	35.16
400.00	522.57	244.46	55.96	544.94	247.26	57.45
500.00	581.74	285.92	82.55	604.73	288.69	84.32
600.00	636.91	319.10	112.87	660.42	321.93	114.91
700.00	688.17	345.69	146.15	712.12	348.63	148.49
800.00	735.79	367.31	181.84	760.14	370.35	184.47
900.00	780.12	385.15	219.49	804.83	388.25	222.43
1000.00	821.49	400.04	258.77	846.53	403.15	262.02

The variation of the thermodynamic functions such as entropy, heat capacity and enthalpy with temperature are graphically represented in Fig.-4. As illustrated in Fig.-4, we can see the increase of calculated thermodynamic functions of m-NAA molecule with temperature. These results compared to those obtained on the para-nitroacetanilide (PNA) molecule are in good agreement.<sup>9</sup> For example, thermodynamic functions obtained at T = 298.15 K on m-NAA molecule using DFT/6-31+G(d) are 479.94 J/mol.K, 196.31 J/mol.K and 34.79 kJ/mol for S, Cp and ddH, respectively. The corresponding

functions obtained at the same temperature (298.15 K) on PNA molecule using DFT/ 6-311+G (d, p) are 447.25 J/mol.K, 184.71 J/mol.K and 32.02 kJ/mol for S, Cp and ddH, respectively. These slight differences may be due to the position of NO<sub>2</sub> moiety in the molecule.

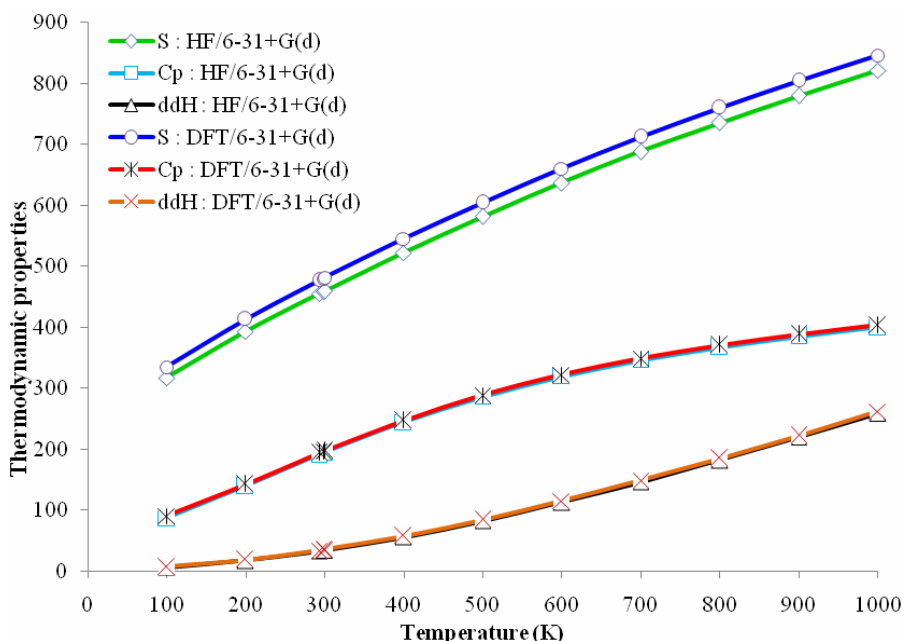


Fig.-4: Correlation graph of thermodynamic parameters of m-nitroacetanilide

## CONCLUSIONS

In this present investigation, we have performed theoretical calculations of molecular electrostatic potential, nonlinear optical properties, HOMO–LUMO and thermodynamic properties for the organic molecule meta-nitroacetanilide (m-NAA). Molecular properties have been calculated by using ab initio HF and DFT (B3LYP) methods with 6-31+G (d) basis set. The molecular electrostatic potential map shows that the negative potential sites are on the electronegative atoms as well as the positive potential sites are around the hydrogen atoms. These sites give information about the possible regions for inter- and intramolecular hydrogen bonding. The calculated dipole moment mean value of m-NAA is 4.65 D which is in agreement with the value (4.9 D) found in literature.<sup>37</sup> The mean polarizability and total first static hyperpolarizability ( $\beta_{\text{total}}$ ) of the molecule is found to be  $17,3437 \times 10^{-23}$  esu and  $5,6419 \times 10^{-30}$  esu, respectively. The  $\beta_{\text{total}}$  value of m-NAA is nearly 29 times more than  $\beta_{\text{total}}$  of urea, inferring that m-NAA molecule to be a potential candidate for nonlinear optical applications. HOMO-LUMO energy gap explains the eventual charge transfer interactions taking place within the molecule. Furthermore, the first-order hyperpolarizability and total dipole moment property of the molecule show that the title molecule is an attractive target for future studies of nonlinear optical properties.

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