

# Quantum Chemical Examination on Structural, Spectroscopic, Population and Molecular Orbitals Analysis of NLO Active 4-Methoxyaniline Hydroquinone for Optoelectronics Applications

V. Siva, A. Shameem, A. Murugan, S. Athimoolam, S. Asath Bahadur

**Abstract.** Quantum chemical calculations of molecular geometry, HOMO-LUMO, Mulliken charge distributions and vibrational assignments of 4-methoxyaniline hydroquinone (4MAHQ) were carried out by DFT (B3LYP) and HF methods. Spectral analysis on 4MAHQ has been studied both by the computational and experimental methods to assign vibrational modes of all the functional groups. The investigation is extensive to calculate the FMOs, population analysis, Molecular Electrostatic Potential and Non Linear Optical efficiency of 4MAHQ. The electron affinity, ionization and chemical potential, electrophilicity index, chemical hardness, electro negativity and global softness of 4-methoxyaniline hydroquinone were calculated by FMO analysis.

**Keywords-** Density Functional theory, HOMO-LUMO, FTIR/FT-Raman, NLO

## I. INTRODUCTION

The increasing demand in optoelectronic device, optical limiter, data processing, optical data storage and telecommunication results in the major development of the design of potentially active nonlinear optical materials. Organic Nonlinear optical materials are found to have certain superior significance when compared to inorganic counterpart due to their higher NLO absorption co-efficient and ultrafast response. Since a long time, Schiff based compounds are generally considered due to their importance in several electro-optical and other technological applications.

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The  $\pi$ -electron conjugation with aromatic structure is essential to exhibit the nonlinear optical (NLO) properties and on this basis the aniline is considered as one of the systems for NLO applications. This statement is substantiated by many theoretical and experimental works.

Some of aniline based NLO materials such as 4-methoxyanilinium trifluoroacetate [11], 4-methyl anilinium p-toluenesulfonate [12], Di-N-methyl anilinium tetrachlorocadmiate(II) [13], anilinium hydrogen sulfate [14], N,N-dimethyl anilinium-3-carboxy-4-hydroxy benzene sulfonate [15], anilinium trichloroacetate [16] anilinium perchlorate [17], 4-chloro anilinium-3-nitrophthalate [18] and 3-nitroanilinium trichloroacetate [19] were studied already and reported for high hyperpolarizability efficiency with good and expected physical and chemical properties. In the present work a novel non-protonation of 4-methoxyaniline hydroquinone has been characterized by quantum chemical methods to study and understand its molecular geometry, population analysis, vibrational and electronic properties.

## II. THEORETICAL CALCULATIONS AND OPTIMIZED GEOMETRY

Theoretical calculation of 4MAHQ is performed from the crystallographic data with HF and DFT methods using GAUSSIAN 09W software package [20]. Crystallographic information data (CIFs) data available in CCDC No.: 1583978 are used for the calculations. Gauss View 05 software [21] is used to obtain the optimized structure, HOMO-LUMO, MEP and vibrational frequency mode of 4MAHQ. The non-proton transfer in 4-methoxyaniline hydroquinone allowed it to crystallize in monoclinic cell with P21/c space group with  $Z=4$ . The inversion centre of the unit cell is occupied with the hydroquinone conformer. The non-proton transfer between the moieties is confirmed from the C-N bond distance of 4-methoxyaniline [1.428(2) Å] and C-O bond distance of hydroquinone [1.375(2) Å]. The planarities of the molecules are confirmed from the torsion angles and these planar molecules are oriented with an angle of 71.03(4) Å to each other (Table I). The optimized 4MAHQ molecular structure is presented in Fig 1.

### III. VIBRATIONAL SPECTRAL ANALYSIS

The Perkin Elmer Spectrometer was used to record the FT-IR spectrum of 4MAHQ in the range 4000–400  $\text{cm}^{-1}$ . BRUKER RFS 27 Raman spectrometer was used to record FT-Raman spectrum in the frequency range 4000-50  $\text{cm}^{-1}$ . Fig. 2 and Fig. 3 represent the experimental and theoretical spectra of 4MAHQ respectively. Theoretical spectra (Table II) were obtained using the B3LYP/HF methods. In aromatic amines, stretching vibration of C-N obtained in 1386–1266  $\text{cm}^{-1}$  [22, 23]. In 4MAHQ, the strong band at 1257  $\text{cm}^{-1}$  may be due to C-N stretching and observed in FT-IR. Stretching vibration of C-N is observed at 1289/1183  $\text{cm}^{-1}$  in HF/DFT Methods and the vibration is not absorbed in FT-Raman spectrum.

Generally in the aromatic compounds C-H stretching vibration is observed in the region 3000–3100  $\text{cm}^{-1}$ . The CH symmetric stretching vibration in FT-Raman observed at 3061 and theoretically at 3312  $\text{cm}^{-1}$  and 3318  $\text{cm}^{-1}$  in B3LYP method and 3172  $\text{cm}^{-1}$  and 3172  $\text{cm}^{-1}$  in HF level. The frequency region 1500–1100  $\text{cm}^{-1}$  in which C-H in-plane bending band and C-C stretching vibrations band interact [24-27]. In experimental, they observed at 1096  $\text{cm}^{-1}$ , 1118  $\text{cm}^{-1}$  as weak bands and the strong peak at 1410  $\text{cm}^{-1}$  in IR spectrum. They also appeared as medium peak at 1174  $\text{cm}^{-1}$  and weak band at 1386  $\text{cm}^{-1}$  in Raman spectrum. Similar vibration was observed at 1098  $\text{cm}^{-1}$ , 1178  $\text{cm}^{-1}$ , 1190  $\text{cm}^{-1}$ , 1271  $\text{cm}^{-1}$ , 1286  $\text{cm}^{-1}$ , 1320  $\text{cm}^{-1}$  and 1405  $\text{cm}^{-1}$  in HF method and 1012  $\text{cm}^{-1}$ , 1124  $\text{cm}^{-1}$ , 1154  $\text{cm}^{-1}$ , 1165  $\text{cm}^{-1}$ , 1195  $\text{cm}^{-1}$ , 1231  $\text{cm}^{-1}$  and 1348  $\text{cm}^{-1}$  in DFT/B3LYP method.

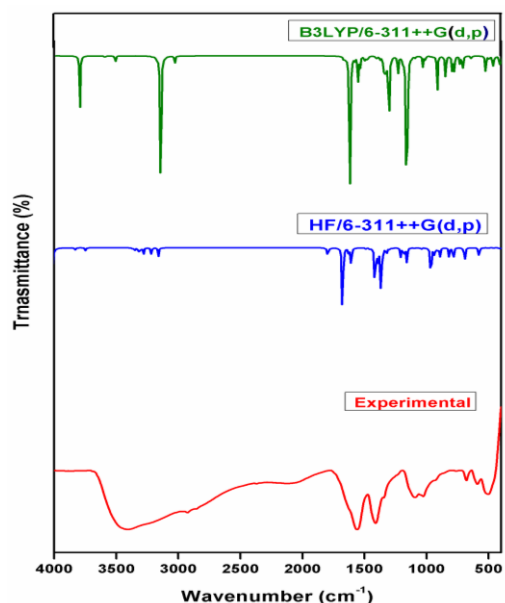


Fig. 2. FTIR spectra of 4MAHQ

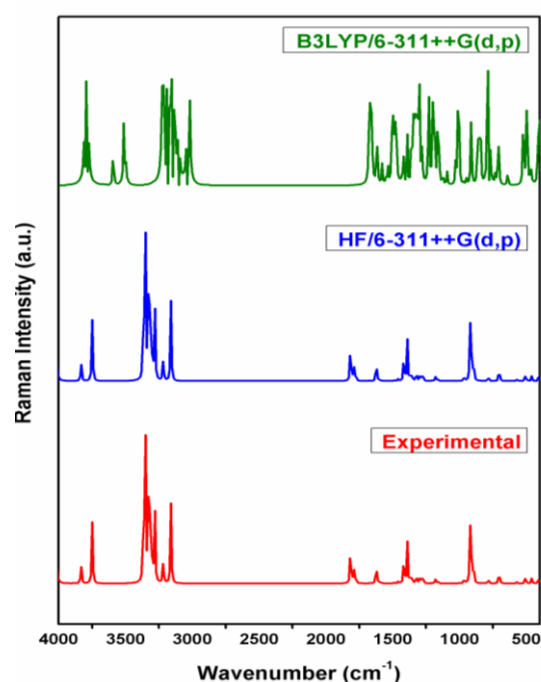
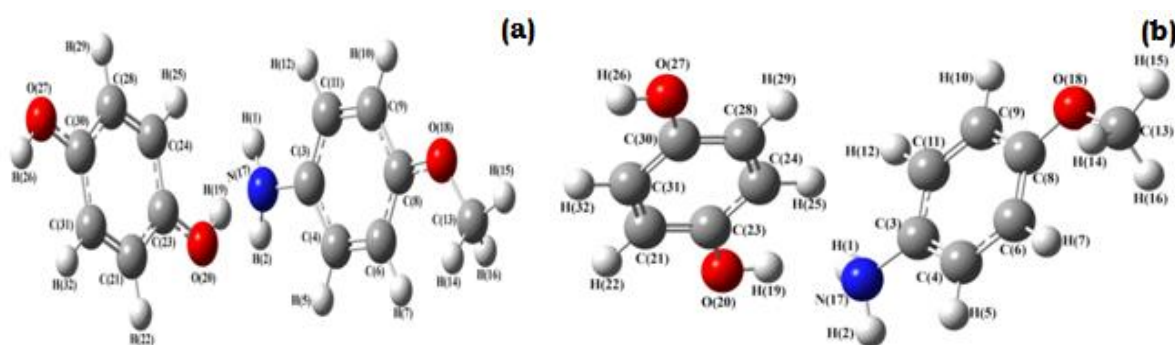


Fig. 3. Raman spectra of 4MAHQ

Table-I: Selected geometrical parameters for 4MAHQ

Atom Connected	Experimental	HF	B3LYP
<i>Bond length (Å)</i>			
H1-N17	0.91(2)	0.999	1.014
H2-N17	0.92(2)	0.999	1.015
C3-C4	1.376(2)	1.379	1.403
C3-C11	1.381(2)	1.394	1.407
C4-H5	0.960	1.077	1.085
C4-C6	1.382(2)	1.393	1.386
C6-H7	0.930	1.073	1.081
C6-C8	1.382(2)	1.381	1.407

Atom Connected	Experimental	HF	B3LYP
C8-C9	1.381(2)	1.392	1.412
C9-H10	0.930	1.074	1.083
C28-C30	1.381(2)	1.382	1.413
C31-H32	0.960	1.078	1.085
<b>Bond Angle (°)</b>			
C4-C3-C11	118.30(1)	118.310	119.288
C4-C3-N17	121.20(1)	121.221	120.285
C11-C3-N17	120.46(1)	120.391	120.346
C3-C4-H5	119.20	119.951	119.840
C3-C4-C6	121.55(2)	121.184	120.760
H5-C4-C6	119.20	118.864	119.401
C8-C9-C11	120.63(2)	120.682	120.359
H10-C9-C11	120.20	120.643	121.244
C3-C11-C9	120.63(1)	120.813	120.326
O27-C30-C31	124.56(1)	122.783	123.173
C28-C30-C31	119.25(2)	119.281	120.263
C21-C31-C30	119.64(2)	120.446	119.805
C21-C31-H32	119.71	119.418	120.226
C30-C31-H32	120.22	120.136	119.969
<b>Torsion Angle (°)</b>			
C11-C3-N17-H2	153.1(1)	154.938	152.791
H2-N17-O20-C23	123.4	123.308	124.94
H22-C21-C23-C24	178.9	179.991	179.699
C31-C21-C23-O20	178.5(2)	179.994	178.303



**Fig. 1. Optimized structure of 4MAHQ a) DFT b) HF**

The medium peak at  $761\text{ cm}^{-1}$  and weak bands at  $880$ ,  $1026\text{ cm}^{-1}$  in IR are assigned to C-H out of plane bending vibrations. This vibration is appeared in Raman spectrum as strong peak at  $839\text{ cm}^{-1}$  and weak bands at  $947$ , and  $980\text{ cm}^{-1}$ . These bands are agreed well with the computed peaks at  $789\text{ cm}^{-1}$ ,  $905\text{ cm}^{-1}$ ,  $936\text{ cm}^{-1}$  and  $1033\text{ cm}^{-1}$  in HF level and  $746\text{ cm}^{-1}$ ,  $803\text{ cm}^{-1}$ ,  $863\text{ cm}^{-1}$  and  $946\text{ cm}^{-1}$  in B3LYP methods, respectively. The C=C and C-C stretching vibrations of benzene ring are expected in the range of  $1400\text{--}1625\text{ cm}^{-1}$  [28]. A sharp peak at  $1560\text{ cm}^{-1}$  in IR spectrum is assigned to C=C stretching vibrations and it is calculated theoretically at  $1585$  by HF and  $1474\text{ cm}^{-1}$  using B3LYP method. C-C stretching band observed at  $1578\text{ cm}^{-1}$  as a

strong peak in Raman spectrum which has good agreement with its theoretical counterpart. The O-H stretching vibration generally expected to occurs at  $3300\text{ cm}^{-1}$ . The O-H in-plane of bending is expected to appear in the range of  $1260\text{--}1440\text{ cm}^{-1}$  [29]. In FT-IR, a band at  $2928\text{ cm}^{-1}$  is assigned to the O-H stretching vibration. This is observed at  $3281\text{ cm}^{-1}$  in HF and  $3142\text{ cm}^{-1}$  in DFT methods. A weak band observed in FT-Raman at  $3294\text{ cm}^{-1}$  is assigned to the O-H stretching vibration.

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The N-H stretching vibrations in amines are expected to occur in the range of 3300–3500  $\text{cm}^{-1}$  [30, 31]. Generally  $\text{NH}_2$  group consists of both asymmetric and symmetric vibrations and the asymmetric vibration frequency is higher than that of symmetric one. The  $\text{NH}_2$  symmetric stretching is observed in IR and Raman bands at 3405  $\text{cm}^{-1}$  and 3061  $\text{cm}^{-1}$ , respectively in the present work. Theoretical peak value is slightly higher and observed respectively at 3832  $\text{cm}^{-1}$ , 3592  $\text{cm}^{-1}$  in IR and Raman. This deviation may be due to the reason that all the theoretical calculation were done in the gaseous state. The asymmetric stretching vibration of  $\text{NH}_2$  obtained at 4020  $\text{cm}^{-1}$  in HF and 3592  $\text{cm}^{-1}$  in B3LYP methods is not observed in the experimental spectra.

The wagging vibration of  $\text{NH}_2$  in aniline derivatives is expected in the range 690–750  $\text{cm}^{-1}$ . For the present compound, it is observed at 678  $\text{cm}^{-1}$  and 761  $\text{cm}^{-1}$  in infrared and 703  $\text{cm}^{-1}$  Raman spectrum. This mode of vibration is observed theoretically at 707 and 709  $\text{cm}^{-1}$  in HF and B3LYP methods respectively. The scissoring mode of  $-\text{NH}_2$  observed at 1605  $\text{cm}^{-1}$ , 1607  $\text{cm}^{-1}$ , 1620  $\text{cm}^{-1}$  in HF level and 1484  $\text{cm}^{-1}$ , 1495  $\text{cm}^{-1}$ , 1498  $\text{cm}^{-1}$  in B3LYP level and absent in infrared and Raman spectra. The weak band observed at 1638  $\text{cm}^{-1}$  in both spectra are due to the scissoring mode of  $-\text{NH}_2$  which are compared with the theoretical values of 1813  $\text{cm}^{-1}$  and 1667  $\text{cm}^{-1}$ . The peaks observed experimentally at 2114  $\text{cm}^{-1}$  and 2454  $\text{cm}^{-1}$  in IR and Raman spectra was assigned to  $\text{NH}_2$  rocking vibration. The corresponding wavenumbers are observed theoretically at 1816  $\text{cm}^{-1}$  in HF and 1669  $\text{cm}^{-1}$  in B3LYP method.

The aromatic stretching vibrations are expected in the frequency range of 1590–1000  $\text{cm}^{-1}$ . In 4MAHQ, this ring stretching vibration band is obtained in theoretically at 1679  $\text{cm}^{-1}$ , 1796  $\text{cm}^{-1}$  and 1538  $\text{cm}^{-1}$ , 1618  $\text{cm}^{-1}$  for the FT-IR and FT-Raman spectra but are not observed in experimental spectra. The mode calculated at 3159  $\text{cm}^{-1}$  in HF and 3029  $\text{cm}^{-1}$  in B3LYP method was assigned to symmetric stretching vibration mode of methoxy group.  $\text{CH}_3$  symmetric stretching vibration is appeared as strong peak in FT-IR at 2845  $\text{cm}^{-1}$  but its asymmetric stretching mode is appeared in Raman at 2854  $\text{cm}^{-1}$ .  $\text{CH}_2$  scissoring vibrations are calculated by theoretical methods at 1459  $\text{cm}^{-1}$  in HF and 1377  $\text{cm}^{-1}$  in B3LYP method.

### IV. POPULATION ANALYSIS

By quantum chemical methods, Mulliken atomic charge distribution was calculated, which has a vital role to the molecular system because atomic charges effect dipole moment, polarizability and electronic structure. The Mulliken charge distribution of the 4MAHQ in HF/B3LYP at 6-311+G(d,p) methods is depicted in Fig. 3. The computed Mulliken charge values are presented in Table III. It is more useful to indicate that the atoms H1, H2, H5, C6, H7, H10, C11, H12, H14, H15, H16, H19, H22, C24, H25, H26, H29, C31 and H32 of 4MAHQ show positive charge, while C3, C4, C8, C9, C13, N17, O18, O20, C21, C23, O27, C28 and C30 atoms show negative charges. The maximum negative charge values are of about 0.4385, 0.5096 in C8 and maximum positive charge values of about 0.4543 and 0.5134 in H19 atoms are obtained at HF and DFT methods respectively

### V. FRONTIER MOLECULAR ORBITAL (FMO) CALCULATIONS

The method of molecular interaction can be predicted by FMOs calculations. Molecular orbital calculations of 4MAHQ are carried out using HF/DFT at 6-311+G(d,p) levels. The molecular energy diagram of 4MAHQ is presented in Fig.4. The Energy gap calculated by taking the energy difference between HOMO and LUMO is an important parameter to indicate the stability of the structure. The calculated HOMO -LUMO energy values of the molecule converted in electronic volts with DFT/ HF levels are -9.297 eV/ -4.561 eV and 0.933 eV/ -7.751 eV. The energy gap value between the molecular orbitals is 4.7358 eV / 6.8044 eV. The HOMO and LUMO energy of 4MAHQ and the electron affinity, ionization and chemical potential, electrophilicity index, chemical hardness, electronegativity and global softness [30] of 4MAHQ is presented in Table IV. The low energy gap is expected for a good NLO active material.

### VI. MOLECULAR ELECTROSTATIC POTENTIAL (MEP) SURFACE ANALYSIS

The reactive behavior of the molecule can be assessed by Molecular electrostatic potential surface analysis in which the negative region is considered as nucleophilic centers and the positive regions are potential electrophilic sites. MEP was calculated at HF/B3LYP with 6-311+G(d,p) of optimized geometries. The MEP maps for positive and negative sites of 4MAHQ are depicted in Fig. 5. The variations of the electrostatic potential at the surface are indicated by different colors and the potential decreases in the order blue > green > orange > red. The red region in MEP surface is the most electronegative region and blue is most positive region whereas the bluish green color surrounded by the ring system of 4MAHQ is related to less positive region. The MEP map of 4MAHQ visibly suggests that the N and O atoms correspond to the most negative (-ve) potential region. The H-atoms is the highest impact of positive(+ve) charges.

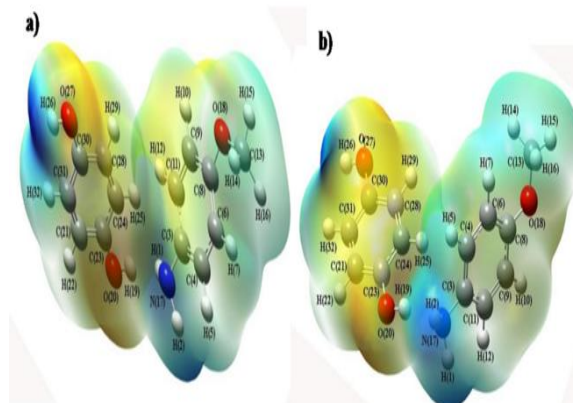


Fig. 6. Electrostatic potential surface of 4MAHQ by (a) HF and (b) B3LYP levels



Table IV: Calculated energy values

Parameters (au)	HF	DFT
$E_{LUMO}$	-0.2848	-0.1676
$E_{HOMO}$	0.0343	-0.3416
$\Delta(E_{LUMO} - E_{HOMO})$	0.25	0.174
Electron Affinity	-0.343	0.1676
Ionization Potential	0.2848	-0.3416
Chemical Hardness	0.159	0.087
Electronegativity	0.125	0.2546
Chemical Potential	-0.125	-0.2546
Electrophilicity Index	0.0491	0.3724
Global softness	1.159	5.747

Table II: Vibrational frequencies and normal mode assignment of 4MAHQ

Mode Number	Observed frequency (cm <sup>-1</sup> )		Calculated frequency (cm <sup>-1</sup> )						Vibrational assignments
			HF			B3LYP			
	IR	Raman	$\nu_{cal}$	$a_I^{IR}$	$b_I^{Raman}$	$\nu_{cal}$	$a_I^{IR}$	$b_I^{Raman}$	
1			9	0.633	2.373	2	0.093	36.485	$\beta(CH)$
2			14	0.059	1.570	15	0.780	71.660	$\gamma(CH)+\omega(CH_3)$
3			18	0.708	7.244	28	1.539	16.074	$\gamma(CH)+\omega(CH \text{ of } CH_3)$
4			39	3.266	1.462	56	0.999	102.598	$\gamma(CH)$
5			53	1.046	1.136	62	15.530	59.755	$\gamma(CH)+\omega(CH \text{ of } CH_3)$
6			71	4.948	0.478	81	2.939	113.069	$\gamma(CH)+\rho(CH_3)$
7			100	0.184	2.407	121	93.270	131.972	$\rho(NH_2+CH_2 \text{ of } CH_3)$
8			170	12.792	0.229	151	2.564	34.799	$(O-H)+\gamma(CH)+\omega(NH \text{ of } NH_2)$
9			183	111.552	1.345	179	111.081	15.910	$t(CH_3)+\omega(NH_2)$
10			184	1.048	1.161	216	29.476	9.632	$t(CH_3)$
11			240	5.094	0.396	225	30.338	20.468	$\delta(NH_2)+\omega(CH \text{ of } CH_3)$

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Mode Number	Observed frequency (cm <sup>-1</sup> )		Calculated frequency (cm <sup>-1</sup> )						Vibrational assignments
			HF			B3LYP			
	IR	Raman	v <sub>cal</sub>	<sup>a</sup> <sub>I</sub> IR	<sup>b</sup> <sub>I</sub> Raman	v <sub>cal</sub>	<sup>a</sup> <sub>I</sub> IR	<sup>b</sup> <sub>I</sub> Raman	
12			251	1.047	0.324	338	4.722	89.587	γ(CH)+ ρ(OH)
13			269	0.220	0.316	354	24.065	14.723	ρ(NH <sub>2</sub> + CH of CH <sub>3</sub> )
14			381	15.128	0.105	358	28.884	35.146	ρ(NH <sub>2</sub> + CH of CH <sub>3</sub> )
15			390	3.329	1.776	370	61.186	4.683	(OH)+ ω(NH <sub>2</sub> )
16			406	0.195	2.493	400	75.530	59.107	γ(CH)+ ρ(OH)
17			408	5.622	2.162	411	126.380	38.338	ρ (NH <sub>2</sub> )+ γ(CH)
18			460	0.330	4.278	414	68.674	21.218	ρ (NH <sub>2</sub> )+ γ(CH)
19			464	0.224	0.120	440	13.798	0.967	β(CH)+ ρ (NH of NH <sub>2</sub> +OH)
20			466	0.297	0.073	459	98.623	5.029	(OH)
21			495	0.202	0.349	466	208.610	19.432	OH+ )+γ(CH) Ring Vib+ ρ(NH of NH <sub>2</sub> )
22	502		506	1.080	7.172	496	60.387	119.771	β(CH)+ ω(NH <sub>2</sub> )
23			569	3.928	1.441	521	80.465	46.904	γ(CH)+ρ (NH <sub>2</sub> )
24			575	14.934	0.012	524	260.528	13.871	γ(CH)+ρ (NH <sub>2</sub> )
25	590		580	38.732	0.092	526	6.553	21.175	β(CH) Ring vibration
26			692	87.288	0.976	639	41.342	12.948	β(CH) Ring vibration
27			702	15.513	4.966	642	22.382	3.434	β(CH) Ring vibration
28	678	703	707	0.606	7.254	709	300.405	60.832	ω (NH <sub>2</sub> )+ γ(CH)+ (OH)
29			781	1.149	1.574	717	3.342	0.410	γ(CH)
30			783	72.769	1.065	731	152.040	11.969	γ(CH)+ ρ(OH+ NH <sub>2</sub> )
31	761		789	18.381	1.087	776	288.548	73.132	γ(CH)
32			818	62.267	0.110	783	83.910	227.923	γ(CH)+ ρ (NH <sub>2</sub> )

Mode Number	Observed frequency (cm <sup>-1</sup> )		Calculated frequency (cm <sup>-1</sup> )						Vibrational assignments
			HF			B3LYP			
	IR	Raman	v <sub>cal</sub>	<sup>a</sup> <sub>I</sub> IR	<sup>b</sup> <sub>I</sub> Raman	v <sub>cal</sub>	<sup>a</sup> <sub>I</sub> IR	<sup>b</sup> <sub>I</sub> Raman	
33		839	891	60.355	9.863	795	268.425	55.807	γ(CH)+ ρ (NH <sub>2</sub> )
34			905	5.032	8.727	803	2.882	0.528	γ(CH)
35	w880		907	9.685	19.674	843	45.192	41.514	γ(CH)
36		w947	915	13.255	7.656	847	143.067	36.871	γ(CH)
37			920	0.993	49.980	849	258.833	10.876	γ(CH)
38			936	70.061	0.073	863	10.465	75.865	γ(CH)+ ω (NH <sub>2</sub> )
39			965	279.099	5.061	914	597.541	72.619	ρ(NH <sub>2</sub> )
40	1026	w982	1033	0.025	0.006	946	26.903	1.614	γ(CH)
41			1043	8.597	0.295	948	0.382	5.983	γ(CH)
42			1067	0.344	0.018	969	9.198	2.664	γ(CH)
43			1078	0.182	0.053	970	1.727	0.209	γ(CH)
44	1096		1097	0.425	0.045	1003	6.945	56.166	β(CH)
45			1098	2.317	0.142	1012	59.895	75.912	β(CH)
46			1157	38.588	1.938	1030	189.066	24.741	β(CH)+ω(CH <sub>3</sub> )+ C-O stretching
47	w1118		1160	66.648	0.092	1094	28.063	15.990	β(CH)+ω (NH <sub>2</sub> )
48		m1174	1178	41.030	5.666	1124	46.306	13.334	β(CH)
49			1190	19.400	0.669	1154	1747.547	45.680	β(CH) Ring breathing
50			1209	63.556	0.485	1161	1.696	1.672	ω(CH <sub>3</sub> )
51			1271	0.582	3.310	1165	1684.452	54.642	β(CH)
52		1257	1279	2.553	2.538	1183	64.617	37.324	C-N
53	w1322		1286	2.364	5.473	1195	122.129	61.069	β(CH)
54		w1288	1301	7.367	4.558	1200	689	87.462	ω(CH <sub>3</sub> )

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55			1320	20.525	2.906	1231	401.533	148.016	$\beta(\text{CH})$
56			1326	25.199	6.071	1280	43.786	48.039	$\beta(\text{CH})$
57			1356	118.401	7.958	1303	1561.449	195.870	C=O Stretching
58	1410	w1386	1370	234.262	3.238	1321	141.682	83.868	$\omega(\text{CH of CH}_3) + \beta(\text{CH})$
59			1390	73.685	43.523	1332	512.401	126.301	$\beta(\text{CH})$ Ring Breathing, C=C
60			1405	103.597	0.686	1348	305.068	97.500	$\beta(\text{CH})$
61			1417	259.467	27.027	1374	59.720	41.060	$\rho(\text{NH of NH}_2) + \beta(\text{CH})$
62			1459	5.603	2.167	1377	10.768	328.076	$\delta(\text{CH}_3)$
63		w1488	1489	6.619	0.819	1403	74.618	394.560	C=O
64	1560	1578	1585	0.522	1.254	1474	57.388	74.436	$\omega(\text{CH of CH}_3) + \text{C=C}$
65			1605	21.354	2.583	1484	70.170	93.296	$\delta(\text{NH}_2) + \beta(\text{CH})$
66			1607	121.791	0.459	1495	12.495	41.523	$\delta(\text{NH}_2)$
67			1620	7.836	12.450	1498	52.570	28.939	$\delta(\text{NH}_2)$
68			1630	27.801	5.824	1504	18.460	88.393	$\beta(\text{CH})$
69			1674	181.842	0.509	1535	162.177	20.181	$\beta(\text{CH})$
70		w1862	1679	321.031	0.263	1538	83.529	6.054	$\beta(\text{CH}) + \text{Ring Vibration}$
71		2092	1776	6.347	7.708	1553	457.976	7.315	C-C+ $\beta(\text{CH}) + \text{Ring Vibration}$
72		2454	1790	1.711	13.136	1580	55.377	27.477	$\beta(\text{CH}) + \text{Ring Breathing}$
73		2608	1796	67.677	5.303	1618	3531.190	77.911	$\beta(\text{CH}) + \text{Ring Breathing}$
74	2114	2528	1816	2.113	20.222	1655	68.032	32.078	$\rho(\text{NH}_2)$
75	2369	2715	1817	3.251	29.023	1669	42.459	478.323	$\rho(\text{NH}_2)$
76			3159	54.382	133.477	3029	124.720	1191.265	O-CH <sub>3</sub> sym stretching
77	s2845	2804	3218	51.666	41.600	3101	14.496	268.309	O-CH <sub>3</sub> Asym stretching
78	m2928	2937	3281	40.653	126.786	3142	3200.506	1210.387	O-H stretching
79			3306	23.173	87.814	3165	7.618	300.277	CH <sub>3</sub> Asym stretching



80			3312	15.201	61.466	3172	23.191	107.027	(C-H) stretching
81			3318	13.016	63.087	3176	11.951	161.650	(C-H) stretching
82			3329	5.985	136.276	3177	14.815	857.812	CH <sub>3</sub> Asym stretching in cation
83			3349	11.408	53.567	3188	1.397	11.230	CH <sub>3</sub> Asym stretching in cation
84			3352	1.405	179.584	3207	2.343	482.489	CH <sub>3</sub> Asym stretching in cation
85			3354	5.248	117.457	3208	2.392	322.371	CH <sub>3</sub> Asym stretching in onion
86			3367	8.113	81.989	3209	3.096	644.397	CH <sub>3</sub> Asym stretching in onion
87			3749	18.662	126.262	3218	6.359	524.093	CH <sub>3</sub> sym stretching in onion
88	s3405	3061	3832	18.000	42.464	3508	127.305	473.000	(NH <sub>2</sub> ) Sym stretching
89			4020	740.562	231.114	3592	29.890	93.051	(NH <sub>2</sub> ) Asym stretching
90			4195	95.022	84.500	3793	881.992	2096.876	O-H

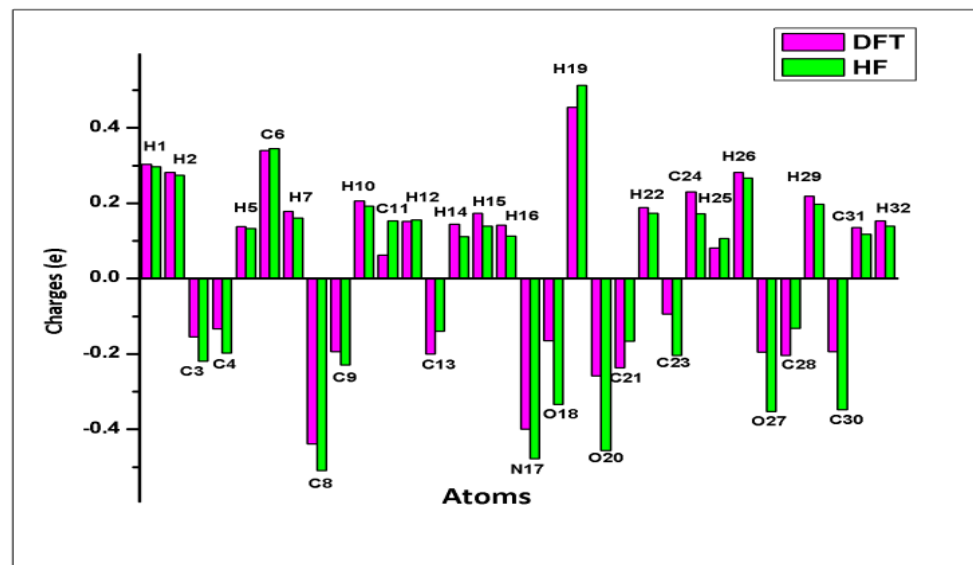


Fig. 4. Mulliken charge distributions for 4MAHQ



$\gamma_{zzyy} + 2\gamma_{zzxx}$  ....(4) The second order hyperpolarizability was calculated for the 4MAHQ structure is  $19.1605 \times 10^{-36}$  esu, this value is nearly 4 times greater than second order hyperpolarizability of Urea(standard). The

Second order hyperpolarizability ( $\gamma$ ) result confirms that the 4MAHQ is a promising material for the optoelectronic device applications.

Table V: Non linear optical parameters of 4MAHQ calculated by DFT/B3LYP

Parameter	a.u	esu ( $\times 10^{-24}$ )	Parameter	a.u	esu ( $\times 10^{-33}$ )	Parameter	a.u	esu ( $10^{-36}$ )
$\mu_x$	-0.8856		$\beta_{xxx}$	-44.7056	-386.225	$\gamma_{xxxx}$	143807	72.29431
$\mu_y$	1.9138		$\beta_{xxy}$	-82.4182	-712.036	$\gamma_{xxyy}$	543.154	0.27357
$\mu_z$	-0.6657		$\beta_{xyy}$	-28.9795	-250.363	$\gamma_{yyyy}$	53267.1	0.26829
$\mu$	2.2113		$\beta_{yyy}$	6.7743	58.52521	$\gamma_{yyzz}$	39619.1	0.19955
$\alpha_{xx}$	5.2572	0.779117	$\beta_{xxx}$	-102.3616	-884.333	$\gamma_{xxzz}$	11469.2	5.77671
$\alpha_{xy}$	13.6126	2.017387	$\beta_{xyz}$	-20.6619	-178.504	$\gamma_{zzzz}$	21323.6	10.74
$\alpha_{yy}$	-85.0716	-12.6076	$\beta_{yyz}$	-1.1741	-10.1434	$\gamma$	64332.1	19.1605
$\alpha_{xz}$	-6.6871	-0.99103	$\beta_{xzz}$	31.7609	274.3919			
$\alpha_{yz}$	1.9712	0.292132	$\beta_{yzz}$	0.7279	6.288546			
$\alpha_{zz}$	-90.0887	-13.3511	$\beta_{zzz}$	3.6077	31.168			
$\alpha$	-56.6343	-8.3932	$\beta_0$	131.7408	1138.148			
$\Delta\alpha$	96.6258	14.3199						

### VIII. CONCLUSION

The molecular structure factors of the 4MAHQ have been optimized at HF/DFT with B3LYP/6-311++G(d,p) and the calculated parameters are in good agreement with experimental single crystal XRD values. The experimental and computed vibrational assignments for 4MAHQ have been reported for the first time. The low energy gap value from FMOs analysis facilitates the charge delocalization in the title compound, which makes the material to be NLO active. Microscopic nonlinear optical parameters have been calculated by DFT. MEP surface gives the visual demonstration of the chemical reactivity of the atoms. The second order hyperpolarizability value is 4 times higher than the standard urea. These above results predict that the 4MAHQ is good nominee for the Optoelectronic applications.

### REFERENCES

- R. Thirumurugan, K. Anitha, Structural, optical, thermal, dielectric, laser damage threshold and Z-scan studies on fumarate salt of creatinine: A promising third-order nonlinear optical material, *Mat. Lett.* 206, 2017, pp. 30-33.
- Siva Vadivel, Asath Bahadur Sultan, Shameem Abdul Samad, Athimoolam Shunmuganarayanan, Raja Muthu., 2018. Synthesis, structural elucidation, thermal, mechanical, linear and nonlinear optical properties of hydrogen bonded organic single crystal guanidinium propionate for optoelectronic device application, *Chem. Phys. Lett.*, 707, 2018, pp. 165–171.
- M. Arockia doss, G.Rajarajan, V.Thanikachalam, S.Selvanayagam, B.Sridhar, Synthesis, spectroscopic (UV–Vis, FT-IR and NMR), single crystal XRD of 3,5-diethyl-2,6-di(thiophen-2-yl)piperidin-4-on-1-ium picrate: A comprehensive experimental and computational study, *J Mol. Struct.*, 1128, 2017, pp.268-278
- F. Helen, G. Kanchana, Growth, mechanical, dielectric, thermal and optical studies of a nonlinear optical crystal: L-Histidinium dipicrate dehydrate, *J Mat. Chem. Phys.* 151 2015, pp. 5-13.

- A. Priyadarshini, S. Kalainathan, Bulk crystal growth, spectral, optical, thermal, electrical and third-order NLO properties of benzylidenemalononitrile derivative single crystal: a promising material for nonlinear optical device applications, *J Mater Sci: Mater Electron.* 29, 2018, pp. 2698–2708.
- K. Ramachandran, Arumugam Raja, V. Mohankumar, Muthu Senthil Pandian, P. Ramasamy, Experimental and theoretical approach of organic 4,4'-dimethylbenzophenone (DMBP) single crystal for NLO application, *Opt. Laser Technol.* 119, 2019, pp.105640.
- V. Siva, A. Shameem, S. Suresh Kumar, M. Raja, S. Athimoolam, S. AsathBahadur., Structural, spectral, Quantum chemical and thermal studies on a new NLO crystal: Guanidinium Cinnamate, *J. Mat. Sci: Mat. Electr.*, 28, 2017, pp. 12484–12496.
- M. Prakash, D. Geetha, M. Lydia Caroline, Crystal growth and characterization of L-phenylalaninium trichloroacetate-A new organic nonlinear optical material, *Physica B.* 406, 2011, pp. 2621-2625.
- M. Suresh, S. Asath Bahadur, and S. Athimoolam, Synthesis, Growth, structural, spectral, thermal and microhardness studies of a new hydrogen bonded organic nonlinear optical material: L-Valinium p -toluenesulfonate monohydrate (LVPT), *J. Mol. Struct.*, 1112, 2016, pp. 71-80.
- P. Karthiga Devi, K. Venkatachalam, Growth, spectroscopic, optical, thermal, dielectric and DFT studies of ammonium picrate: a nonlinear optical crystal, *J. Mat. Sci.: Mat. Electron.*, (8) 27 (2016) pp. 8590–8598.
- V. Siva, S. Suresh Kumar, M. Suresh, M. Raja, S. Athimoolam, S. Asath Bahadur, N–H...O hydrogen bonded novel nonlinear optical semiorganic crystal (4-methoxyanilinium trifluoroacetate) studied through theoretical and experimental methods, *J. Mol. Struct.* 1133, 2017, pp. 163-171
- G. Shanmugam, S. Brahadeeswaran, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 95, 2012, pp. 177–183.
- T. Dhanabal, G. Amirthaganesan, Growth, spectral, thermal and dielectric studies on a new semiorganic NLO material: Di-N-methylanilinium tetrachlorocadmiate (II), *Optik*, 125, 2014, pp. 238–242.
- N. Sudharsana, G. Subramanian, V. Krishnakumar, R. Nagalakshmi, Growth and characterization of anilinium hydrogen sulfate (AHS) single crystals: An organic nonlinear optical material, *Spectrochimica Acta Part A*, 97, 2012, pp. 798–805.
- M. Rajkumar, A. Chandramohan Synthesis, growth, characterisation and laser damage threshold studies of

# Quantum Chemical Examination on Structural, Spectroscopic, Population and Molecular Orbitals Analysis of NLO Active 4-Methoxyaniline Hydroquinone for Optoelectronics Applications

- N,N-dimethylanilinium-3-carboxy-4-hydroxyl benzene sulphonate crystal: An efficient SHG material for electro-optic applications, *Opt. Mater.* 66,2017, pp. 261-270.
16. H. Tanak, K. Pawlus, M.K. Marchewka, A. Pietraszko, Structural, vibrational and theoretical studies of aniliniumtrichloroacetate: New hydrogen bonded molecular crystal with nonlinear optical properties, *Spectrochimica Acta Part A*, 118, 2014, pp. 82-93
  17. P. Vivek, A. Suvitha, P. Murugakoothan, Growth, spectral, anisotropic, second and third order nonlinear optical studies on potential nonlinear optical crystal anilinium perchlorate (AP) for NLO device fabrications, *Spectrochimica Acta Part A*, 134, 2015, pp.517-525.
  18. K. Singaravelan, A. Chandramohan, M. Saravanabhavan, I.V. Muthu Vijayan Enoch, V.S. Suganthi, Hydrogen bonded charge transfer molecular salt (4-chloro anilinium-3-nitrophthalate) for photophysical and pharmacological applications, *Spectrochimica Acta Part A* 5;184, 2017, pp. 318-326.
  19. E. Selvakumar, A. Chandramohan, G. AnandhaBabu, P. Ramasamy Synthesis, growth, structural, optical and thermal properties of a new organic salt crystal: 3-nitroanilinium trichloroacetate, *J.Crystal Growth* 401, 2014, pp. 323-326.
  20. M.J. Frisch et al., Gaussian Inc., Wallingford, CT, 2009.
  21. R. Dennington, T. Keith, J. Millam. Gauss View, Version 5.0.8 Semichem Inc., Shawnee Mission KS. 2013.
  22. R.M. Silverstein, F.X. Webster, *Spectrometric Identification of Organic Compounds*, sixth ed., John Wiley, Inc., New York. 2003.
  23. G. Socrates, *Infrared and Raman Characteristic Wavenumbers*, third ed., John Wiley & Sons, Limited, Chichester, 2001.
  24. W. O. George, P. S. McIntyre, *Infrared Spectroscopy*, John Wiley and Sons, London, 1987.
  25. R. L. Peesole, L. D. Shield, I.C. McWilliam, *Modern Methods of Chemical Analysis*, Wiley, New York, (1976).
  26. V. Krishnakumar, V. Balachandran, T. Chitham barathann, DFT studies, vibrational spectra and conformational stability of 4-hydroxy -3-methyl acetophenone and 4-hydroxy- 3-methoxy acetophenone, *Spectrochim. Acta Part A*, 62,2005, pp.918-925.
  27. M. Divya Bharathi, R. Bhuvaneswari, J. Srividya, G. Vinitha, R.N.Prithiviraaja, G.Anbalagan, Synthesis, optical, experimental and theoretical investigation of third order nonlinear optical properties of 8-hydroxyquinolinium 2-carboxy-6-nitrophthalate monohydrate single crystal, *J. Phys.. Chem. Solid*, 113, 2016, pp. 50-60
  28. D. N. Sathyanarayana, *Vibrational Spectroscopy -Theory and Applications*, second ed., New Age International (P) Limited Publishers, New Delhi, 2004.
  29. A. Anandhan, C. Sivasankari, M. Saravanabhavan, V. Siva, K. Senthil, Synthesis, crystal structure, spectroscopic investigations, physicochemical properties of third order NLO single crystal for optical applications, *J. Mol. Struct.* 2019, pp.127400.
  30. J. Thomas Prakash, S. Kumararaman, Growth and characterization of L-proline cadmium chloride monohydrate single crystals, *Mater. Lett.* 62, 2008, pp.4097-4099.

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