

# Vibrational Spectra and Potential Energy Distributions for 5-Chloro-2-nitroanisole by Density Functional Theory and Normal Coordinate Calculations

G. VENKATESH<sup>1,\*</sup>, M. GOVINDARAJU<sup>2</sup> and P. VENNILA<sup>3</sup>

<sup>1</sup>Research and Development Centre, Bharathiar University, Coimbatore-641 046, India <sup>2</sup>Department of Chemistry, Arignar Anna Government Arts College, Namakkal-638 052, India <sup>3</sup>Department of Chemistry, Thiruvalluvar Government Arts College, Rasipuram-637 401, India

\*Corresponding author: E-mail: venkateshindhuja@gmail.com

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In this study, the vibrational spectral analysis have been carried out using FT-IR and FT-Raman spectroscopy in the regions of 4000-400 cm<sup>-1</sup> and 3500-100 cm<sup>-1</sup>, respectively for 5-chloro-2-nitroanisole (5C2NA). The molecular geometry and vibrational frequencies of 5-chloro-2-nitroanisole were estimated by applying the density functional theory approaches including 6-31G\*/6-311+G\*\* as basis set. The variation between the observed and scaled wave number values of most of the basics is very small. Coupling of vibrations has been decided by reckoning total energy distributions. FT-IR and FT-Raman spectra of the 5-chloro-2-nitroanisole have been calculated. Further, density functional theory combined with quantum chemical calculations to find out the first-order hyperpolarizability. The calculated HOMO-LUMO energy gap shows that charge transfer occurs inside the molecule. Electronic excitation energies, oscillator strength and character of the respective excited states were calculated by the closed-shell singlet calculation method for the molecule.

Keywords: 5-Chloro-2-nitroanisole, DFT, FT-Raman, FT-IR, Hyperpolarizability, Electronic excitation energy.

## **INTRODUCTION**

Anisole is a forerunner to perfumes, insect pheromones and pharmaceuticals [1]. Anisole is a solvent used in the amalgamation of organic compounds and in large-scale applications such as the making of perfumes. Anisole has been used directly in the synthesis of the marine pyrrole alkaloids. It may also be employed in the making of inorganic complexes and resources, such as tin-core and tin oxide nanoparticles. It is often used in the solid-phase synthesis of compounds, principally in the division of compounds from the resin. 5-chloro-2-nitroanisole is mixed up in the synthesis of orally bio-available anaplastic lymphoma kinases (ALK) inhibitors as anticancer drugs. In addition, it is used in the amalgamation of kinesin spindle protein (KSP) inhibitors which are liable for the spindle pole division which occurs during mitosis in cancer cells.

The vibrational studies of these molecules would be supportive in understanding the different types of bonding and usual modes of vibrations involved in these systems. The computational methods of vibrational spectroscopy [2,3] changed remarkably when quantum mechanical programs for optimization of the geometry of a molecule and for analytical determination of its force field appeared. Harmonic force fields derived from quantum mechanics are widely used for the calculation of frequencies and the modes of normal vibrations.

In our study, the vibrational spectra of 5-chloro-2nitroanisole (5C2NA) by applying the density functional theory (DFT) calculations based on Beck3-Lee-Yang-Parr (B3LYP) level with the use of the standard 6-311+G\*\* basis sets. The calculated vibrational frequencies were compared with obtained experimental results and simulated and the observed spectra were also analyzed.

# **EXPERIMENTAL**

The 5-chloro-2-nitroanisole (5C2NA) was obtained from Aldrich chemicals USA. The Fourier transform infrared spectra of the title compounds were calculated in the region 4000-400 cm<sup>-1</sup>, at a resolution of  $\pm 1$  cm<sup>-1</sup>, using BRUKER IFS 66V vacuum Fourier convert spectrometer, equipped with an MCT detector, a KBr beam splitter and global source. The FT-Raman spectra were documented on the same instrument with FRA 106 Raman accessories in the region 4000-100 cm<sup>-1</sup>. Nd: YAG laser operating at 200 mW power with 1064 nm excitation was used as source.

# **COMPUTATIONAL METHODS**

The entire calculations were carried to GAUSSIAN 09W program package [4] and the vibrational modes were assigned by means of visual inspection using GAUSSVIEW program. The geometry optimization and energy calculations of 5-chloro-2-nitroanisole were carried out using DFT (B3LYP) methods [5,6] with 6-31G\*/6-311+G\*\* basis sets, correspondingly. The Cartesian representation of the theoretical force constants have been computed at optimized geometry by assuming C<sub>s</sub> point group symmetry, scaling of the force fields were performed by the scaled quantum mechanical procedure [7]. To achieve a close agreement between the observed and calculated frequencies, least-square fit refinement algorithm was used. The force field gained by this way was then used to recalculate the usual modes, total energy distributions and the corresponding theoretically anticipated IR and Raman intensities to predict the full IR and Raman spectra of 5-chloro-2-nitroanisole.

The prediction of Raman intensities was carried out by following the method outlined below. The Raman activities (Si) calculated by the GAUSSIAN 09W program are adjusted during scaling procedure with MOLVIB were improved to relative Raman intensities ( $I_i$ ) using the following relationship derived from the basic theory of Raman scattering [8,9].

$$I_{i} = \frac{f(v_{o} - v_{i})^{4} S_{i}}{v_{i} [1 - \exp(-hc v_{i} / KT)]}$$
(1)

where  $v_0$  is the exciting frequency (cm<sup>-1</sup>),  $u_i$  is the vibrational wavenumber of the usual mode; h, c and k are universal constants and f is a duly chosen general normalization factor for all peak intensities.

# **RESULTS AND DISCUSSION**

**Molecular geometry:** The optimized molecular structure of the 5C2NA having C<sub>s</sub> point group of symmetry is exposed in Fig. 1. The global minimum energy obtained by the DFT structure optimization was presented in Table-1. The most optimized structural parameters were also calculated and shown in Table-2.



Fig. 1. Optimized molecular structure of 5C2NA

Method	Energies (Hartrees)
6-31G*	-1010.659246
6-311+G**	-1010.85618

The molecule 5C2NA belongs to the C<sub>s</sub> point group symmetry. The 18 atoms of the title compound gives increase to 48 normal modes of vibrations and they are distributed among the symmetry species as  $\Gamma_{3N-6} = 33 \text{ A}' + 15 \text{ A}''$ . The A' and A'' represents the in-plane and out-of-plane vibrations, correspondingly. All the vibrations were active both in Raman scattering and infrared absorption.

**Analysis of vibrational spectra:** Detailed description of vibrational modes can be given by means of usual coordinate analysis (NCA). For this reason, the full set of 62 standard inner coordinates containing 14 redundancies were defined as given in Table-3. From these, a non-redundant set of local symmetry coordinates were constructed by suitable linear combinations of internal coordinates following the recommendations of Fogarasi *et al.* [10] are summarized in Table-4. The theoretically calculated

TABLE-2
OPTIMIZED GEOMETRICAL PARAMETERS OF 5C2NA OBTAINED BY B3LYP/ 6-311+G** DENSITY FUNCTIONAL CALCULATIONS

Bond length	Value (Å)	Bond angle	Value (Å)	Dihedral angle	Value (Å)
C2-C1	1.38599	C3-C2-C1	119.9995	C4-C3-C2-C1	0
C3-C2	1.38607	C4-C3-C2	120.0002	C5-C4-C3-C2	0
C4-C3	1.38600	C5-C4-C3	120.0002	C6-C5-C4-C3	0
C5-C4	1.38599	C6-C5-C4	119.9995	O7-C1-C2-C3	-179.42757
C6-C5	1.41005	O7-C1-C2	119.9986	N8-C2-C1-C6	-179.42810
O7-C1	1.44605	N8-C2-C1	119.9966	H9-C3-C2-C1	-179.42859
N8-C2	1.12205	H9-C3-C2	119.9993	H10-C4-C3-C2	-179.42806
H9-C3	1.12205	H10-C4-C3	119.9999	Cl11-C5-C4-C3	-179.42864
H10-C4	1.76006	Cl11-C5-C4	119.9983	H12-C6-C5-C4	-179.42805
Cl11-C5	1.12205	H12-C6-C5	119.9990	C13-07-C1-C2	119.99995
H12-C6	1.41003	C13-07-C1	109.4966	014-N8-C2-C1	-180
C13-07	1.13174	014-N8-C2	120.0005	O15-N8-C2-C1	0.57437
014-N8	1.31602	O15-N8-C2	119.9981	H16-C13-07-C1	180
O15-N8	1.12205	H16-C13-07	109.4964	H17-C13-07-C1	59.92832
H16-C13	1.12192	H17-C13-07	109.4981	H18-C13-07-C1	-59.9305
H17-C13	1.12191	H18-C13-07	109.4996		
H18-C13	1.12173				
	a —				

\*for numbering of atom refer Fig. 1

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TABLE-3 DEFINITION OF INTERNAL COORDINATES OF 5C2NA				
No(i)	Symbol	Туре	Definition	
Stretching	•			
1-6	r <sub>i</sub>	C-C	C1-C2,C2-C3,C3-C4,C4-C5,C5-C6,C6-C1	
7-9	$S_i$	C-H	C3-H9,C4-H10,C6-H12	
10-11	$p_i$	C-O	C1-07,C13-07	
12	$P_i$	C-N	C2-N8	
13	R <sub>i</sub>	C-Cl	C5-Cl11	
14-15	$\pi_{i}$	N-O	N8-014,N8-015	
16-18	n <sub>i</sub>	C-H(m)	C13-H16,C13-H17,C13-H18	
Bending				
19-24	α <sub>i</sub>	C-C-C	C1-C2-C3,C2-C3-C4,C3-C4-C5,C4-C5-C6,C5-C6-C1,C6-C1-C2	
25-30	$\theta_{i}$	C-C-H	C2-C3-H9,C4-C3-H9,C3-C4-H10,C5-C4-H10, C5-C6-H12,C1-C6-H12	
31-32	$\beta_i$	C-C-Cl	C4-C5-C111, C6-C5-C111	
33-34	$\mathbf{\Phi}_{\mathrm{i}}$	C-C-O	C2-C1-O7, C6-C1-O7	
35	$\gamma_{i}$	C-O-C	C1-07-C13	
36-37	$\mu_{i}$	C-C-N	C3-C2-N8, C1-C2-N8	
38	$ ho_{ m i}$	O-N-O	O14-N8-O15	
39-40	$\lambda_{i}$	C-N-O	C2-N8-O14,C2-N8-O15	
41-43	$\nu_{i}$	H-C-H	H16-C13-H17,H17-C13-H18,H18-C13-H16	
44-46	φ <sub>i</sub>	O-C-H	O7-C13-H16,O7-C13-H17,O7-C13-H18	
Out-of-plane				
47-49	ω <sub>i</sub>	C-H	H9-C3-C2-C4,H10-C4-C3-C5, H12-C6-C5-C1	
50	ξi	C-Cl	Cl11-C5-C6-C4	
51	$\Omega_{i}$	C-O	07-C1-C2-C6	
52	ត្	C-N	N8-C2-C3-C1	
53	$\eta_i$	C-N-O	C2-N8-014-015	
Torsion	14			
54-59	$\tau_{i}$	τC-C	C1-C2-C3-C4,C2-C3-C4-C5,C3-C4-C5-C6,C4-C5-C6-C1,C5-C6-C1-C2,C6-C1-C2,C3	
60	τ	τC-O(m)	C2(C6)-C1-O7-C13	
61	τ,	τCH <sub>3</sub>	C1-O7-C13-(H16, H17,H18)	
62	τ,	τΝΟ	C3(C1)-C2-N8-O14(O15)	

TABLE-4 DEFINITION OF LOCAL SYMMETRY COORDINATES AND THE VALUE CORRESPONDING SCALE FACTORS USED TO CORRECT THE FORCE FIELDS FOR 5C2NA					
No.(i)	Symbol <sup>a</sup>	Definition <sup>b</sup>	Scale factors used in calculation		
1-6	C-C	r1, r2, r3, r4, r5, r6	0.914		
7-9	C-H	S7, S8, S9	0.914		
10-11	C-O	p10, p11	0.992		
12	C-N	P12	0.992		
13	C-Cl	R13	0.992		
14-15	N-O	π14, π15	0.992		
16	mss	(n16+n17+n18)/√3	0.995		
17	mips	(2n17-n16-n18)/√6	0.992		
18	mops	(n17-n18)/√2	0.919		
19	C-C-C	$(\alpha 19 - \alpha 20 + \alpha 21 - \alpha 22 + \alpha 23 - \alpha 24)/\sqrt{6}$	0.992		
20	C-C-C	$(2\alpha 19 - \alpha 20 - \alpha 21 + 2\alpha 22 - \alpha 23 - \alpha 24)/\sqrt{12}$	0.992		
21	C-C-C	$(\alpha 20 - \alpha 21 + \alpha 23 - \alpha 24)/2$	0.992		
22-24	C-C-H	$(\theta 25 - \theta 26)/\sqrt{2}, (\theta 27 - \theta 28)/\sqrt{2}, (\theta 29 - \theta 30)/\sqrt{2}$	0.916		
25	C-C-Cl	(β31-β32)/√2	0.923		
26	C-C-O	(Φ33-Φ34)/√2	0.923		
27	C-O-C	γ35	0.990		
28	C-C-N	(µ36-µ37)/√2	0.990		
29	O-N-O	p38	0.923		
30	C-N-O	(λ39-λ40)/√2	0.923		
31	msb	(v41+v42+v43-φ44-φ45-φ46)/√6	0.990		
32	mipb	(2v43-v41-v42)/√ 6	0.990		
33	mopb	(v41-v43)/√2	0.990		
34	mipr	(2φ45-φ44-φ46)/√6	0.990		
35	mopr	(φ44-φ46)/√2	0.990		

$36-38$ C-H $\omega 47, \omega 48, \omega 49$ $0.994$ $39$ C-CI $\xi 50$ $0.962$ $40$ C-O $\Omega 51$ $0.962$ $41$ C-N $\omega 52$ $0.962$ $42$ C-N-O $\eta 53$ $0.963$ $43$ tring $(\tau 54 - \tau 55 + \tau 56 - \tau 57 + \tau 58 - \tau 59)/\sqrt{6}$ $0.994$ $44$ tring $(\tau 54 - \tau 55 + \tau 56 - \tau 57 + \tau 58 - \tau 59)/\sqrt{12}$ $0.994$ $45$ tring $(\tau 54 + 2 \tau 55 - \tau 56 - \tau 57 + 2 \tau 58 - \tau 59)/\sqrt{12}$ $0.994$ $46$ C-O $\tau 60/2$ $0.979$ $47$ OCH <sub>3</sub> $\tau 61/3$ $0.979$ $48$ N-Q $\tau 62/2$ $0.979$				
39C-Cl $\xi50$ 0.96240C-O $\Omega51$ 0.96241C-N $\omega52$ 0.96242C-N-O $\eta53$ 0.96343tring $(t54-t55+t56-t57+t58-t59)/\sqrt{6}$ 0.99444tring $(t54-t56+t57-t59)/2$ 0.99445tring $(-t54+2t55-t56-t57+2t58-t59)/\sqrt{12}$ 0.99446C-O $t60/2$ 0.97947OCH <sub>3</sub> $t61/3$ 0.97948N-O $t62/2$ 0.979	36-38	С-Н	ω47, ω48, ω49	0.994
40C-OΩ510.96241C-Nω520.96242C-N-Oη530.96343tring $(\tau54 + \tau55 + \tau56 + \tau57 + \tau58 + \tau59)/\sqrt{6}$ 0.99444tring $(\tau54 + \tau56 + \tau57 + \tau58 + \tau59)/\sqrt{12}$ 0.99445tring $(-\tau54 + 2\tau55 + \tau56 + \tau57 + 2\tau58 + \tau59)/\sqrt{12}$ 0.99446C-O $\tau60/2$ 0.97947OCH <sub>3</sub> $\tau61/3$ 0.97948N-Q $\tau62/2$ 0.979	39	C-Cl	ξ50	0.962
41C-N $\omega 52$ 0.96242C-N-O $\eta 53$ 0.96343tring $(\tau 54 - \tau 55 + \tau 56 - \tau 57 + \tau 58 - \tau 59)/\sqrt{6}$ 0.99444tring $(\tau 54 - \tau 56 + \tau 57 - \tau 59)/\sqrt{2}$ 0.99445tring $(-\tau 54 + 2 \tau 55 - \tau 56 - \tau 57 + 2 \tau 58 - \tau 59)/\sqrt{12}$ 0.99446C-O $\tau 60/2$ 0.97947OCH <sub>3</sub> $\tau 61/3$ 0.97948N-Q $\tau 62/2$ 0.979	40	C-0	Ω51	0.962
42C-N-O $\eta 53$ 0.96343tring $(\tau 54 - \tau 55 + \tau 56 - \tau 57 + \tau 58 - \tau 59)/\sqrt{6}$ 0.99444tring $(\tau 54 - \tau 56 + \tau 57 - \tau 59)/2$ 0.99445tring $(-\tau 54 + 2 \tau 55 - \tau 56 - \tau 57 + 2 \tau 58 - \tau 59)/\sqrt{12}$ 0.99446C-O $\tau 60/2$ 0.97947OCH <sub>3</sub> $\tau 61/3$ 0.97948N-Q $\tau 62/2$ 0.979	41	C-N	ω52	0.962
43tring $(t54-t55+t56-t57+t58-t59)/\sqrt{6}$ 0.99444tring $(t54-t56+t57-t59)/2$ 0.99445tring $(-t54+2t55-t56-t57+2t58-t59)/\sqrt{12}$ 0.99446C-O $t60/2$ 0.97947OCH <sub>3</sub> $t61/3$ 0.97948N-Q $t62/2$ 0.979	42	C-N-O	η53	0.963
44tring $(\tau54-\tau56+\tau57-\tau59)/2$ 0.99445tring $(-\tau54+2\tau55-\tau56-\tau57+2\tau58-\tau59)/\sqrt{12}$ 0.99446C-O $\tau60/2$ 0.97947OCH3 $\tau61/3$ 0.97948N-Q $\tau62/2$ 0.979	43	tring	(154-155+156-157+158-159)/16	0.994
45tring $(-\tau54+2\tau55-\tau56-\tau57+2\tau58-\tau59)/\sqrt{12}$ 0.99446C-O $\tau60/2$ 0.97947OCH3 $\tau61/3$ 0.97948N-Q $\tau62/2$ 0.979	44	tring	(154-156+157-159)/2	0.994
46C-O $\tau 60/2$ 0.97947OCH3 $\tau 61/3$ 0.97948N-O $\tau 62/2$ 0.979	45	tring	(-τ54+2τ55-τ56-τ57+2τ58-τ59)/√12	0.994
$\begin{array}{cccc} 47 & OCH_3 & \tau 61/3 & 0.979 \\ 48 & N-Q & \tau 62/2 & 0.979 \end{array}$	46	C-0	τ60/2	0.979
48 N-O <u>762/2</u> 0.979	47	OCH <sub>3</sub>	τ61/3	0.979
	48	N-O	τ62/2	0.979

<sup>a</sup>These symbols are used for description of the normal modes by TED in Table-5.

<sup>b</sup>The internal coordinates used here are defined in Table-3.

DFT force fields were transformed in this later set of vibrational coordinates and used in all subsequent calculations. The detailed vibrational assignments of fundamental modes of 5C2NA along with calculated IR, Raman intensities and normal mode descriptions were reported in Table-5. For visual comparison, the observed and simulated FT-IR and FT-Raman spectra of 5C2NA are produced in a general frequency scales in Figs. 2 and 3. When using computational methods to predict theoretical normal vibrations for relatively complex, scaling factors are used to bring computed wavenumbers into nearer agreement with observed frequencies for the DFT method employed in this work the simplest limiting scaling factors was used.

Root mean square (RMS) values of frequencies were obtained in the study using the subsequent expression:

$$RMS = \sqrt{\frac{1}{n-1}\sum_{i}^{n}(v_{i}^{calc} - v_{i}^{exp})^{2}}$$

The RMS fault of the frequencies (unscaled) observed for 5C2NA are found to be 98 cm<sup>-1</sup>, correspondingly. In order to reproduce the observed frequencies, improvement of scaling factors were applied and optimized *via* least square refinement algorithm which resulted a weighted RMS deviation of 7.7



Fig. 2. FT-IR spectra of 5C2NA (a) Calculated (b) Observed with B3LYP/ 6-311+G\*\*



Fig. 3. FT-Raman spectra of 5C2NA (a) Calculated (b) Observed with B3LYP/6-311+G\*\*  $\,$ 

cm<sup>-1</sup> between the experimental and scaled quantum mechanical (SQM) frequencies for B3LYP/6-311+G\*\* basis sets.

**C-H vibrations:** Aromatic compounds have have three or four peaks in the region 3300-3100 cm<sup>-1</sup>. These are due to the stretching vibrations of the ring C-H bands. In the present study, the FT-IR bands recognized at 3254, 3252, 3249 cm<sup>-1</sup> and FT Raman bands at 3238, 3237 and 3236 cm<sup>-1</sup> are assigned to C-H stretching vibrations of 5C2NA which are in good agreement with calculated values by B3LYP/6-311+G\*\*. The C-H out-of-plane bending vibrations of the 5C2NA are indentified at 853, 851 and 847 cm<sup>-1</sup> in the FT-IR and 846, 843, 840 cm<sup>-1</sup> in the FT-Raman spectra which are bring into being to be well within their characteristic region [11].

**C-C vibrations:** The bands between 1680-1400 cm<sup>-1</sup> are assigned to C-C stretching modes [12]. Hence, in the present study, the carbon-carbon vibrations of the 5C2NA compound are observed at 1636, 1634, 1630, 1495, 1493 and 1490 cm<sup>-1</sup> in the FT-IR spectrum and 1668, 1665, 1662, 1612, 1610, 1608, 1527 and 1523 cm<sup>-1</sup> in the FT-Raman.

**Ring vibrations:** The benzene ring modes primarily involve C-C bonds. In the present study, the bands attributed at 905, 904, 901, 726, 725, 722 and 890, 889, 887, 696, 694, 692, 635, 634, 631 cm<sup>-1</sup> for 5C2NA have been designated to ring in-plane and out-of plane bending modes respectively. The

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#### TABLE-5 DETAILED ASSIGNMENTS OF FUNDAMENTAL VIBRATIONS OF 5C2NA BY NORMAL MODE ANALYSIS BASED ON SQM FORCE FIELD CALCULATION

C	<b>G</b> (	Obs	erved	Calculated frequency (cm <sup>-1</sup> ) with		with		
S. No	symmetry	nequen	cy (cm )	DOL	,1P/0-311-		Demen	• TED (%) among type of internal coordinates <sup>c</sup>
INO.	species C <sub>s</sub>	IR	Raman	Unscaled	Scaled	IR. A	Raman	
1	Δ'	3254		3252	32/0	25 351	63 710	CH(00)
2	A'	5254	2227	3232	3249	1 154	116 460	CH(00)
2	A \	3240	5257	3230	3230	0.405	58 010	CH(00)
1	A \	5240	2170	3239	3233	0.403	55 484	$\operatorname{mons}(00)$ mins(7)
	A'		5179	2125	2122	15 510	78 005	mops(90), mips(7) mins(78), mass(11), mans(10)
5	A	2050		2040	2046	13.310	78.005	mps(78), mss(11), mops(10)
0	A	3030	1665	3049	3040	49.388	94.152	mss(64), mps(15) GG(2(1), NO(2)(25), h GGN(7), h NO(2)(7), h diversion (5), h GH(5), h GH
/	A	1(2)	1005	1008	1602	245.001	19.081	CC(50), $NOas(53)$ , $bCCN(7)$ , $bNO2r(7)$ , $bring(3)$ , $bCH(5)$
8	A	1030	1(1)	1634	1030	139.271	75.029	CC(51), $NOas(23)$ , $bCH(13)$ , $bring(8)$
9	A	1526	1612	1610	1607	55.378	20.001	CC(56), $NOas(24)$ , $bring(8)$ , $bCH(6)$
10	A'	1536	1505	1539	1534	10.965	14.675	bmipb(71), bmopb(27)
11	A'		1527	1526	1523	32.752	11.084	bCH(30), CC(28), bmsb(25), CO(9)
12	A'			1519	1514	25.911	12.522	bmopb(75), bmipb(22)
13	A'	1495		1493	1490	27.130	5.326	bmsb(53), bCH(18), CC(15), bmopb(5)
14	A'		1440	1438	1436	73.090	15.787	CC(42), bCH(17), bmsb(10), CO(9)
15	A'			1401	1399	257.394	173.334	NOss(63), CN(15), bNO2sc(14)
16	A'	1355		1353	1350	1.817	4.205	CC(84), bCH(10)
17	A'		1283	1280	1278	113.994	41.827	CO(46), CC(20), bring(8), bCH(8)
18	A'	1278		1276	1274	35.395	5.364	bCH(62), CC(25), bCO(6)
19	A'		1217	1220	1216	9.377	7.056	bmopr(58), bmipr(24)
20	A'			1186	1183	4.147	5.908	bCH(49), CC(29), CN(9)
21	A'	1179		1180	1177	2.654	9.162	bmipr(50), bmopr(22), bmopb(13), bmipb(10)
22	A'		1132	1130	1127	5.326	7.239	bCH(29), bring(23), CC(20), CN(16)
23	A'	1106		1105	1102	59.803	35.588	CC(48), bCH(16), Cl(12), bring(8), CN(6), CO(6)
24	A'			1045	1042	118.659	12.154	CO(67), bring(18)
25	A'		975	973	970	1.428	0.927	bCH(86), tring(11)
26	A'	904		905	901	81.760	1.555	bring(28), gCH(17), CO(15), Cl(12), tring(6)
27	A'		890	889	887	22.848	1.573	bCH(62), tring(16)
28	A''	853		851	847	17.840	4.745	gCH(47), bNO2sc(15), gCN(8), tring(8)
29	A''		843	846	840	12.041	7.598	gCH(31), bNO2sc(27), CC(7), CO(6)
30	A''			776	771	15.902	1.577	tring(25), gCNO(25), gCN(16), gCH(15), gCO(11)
31	A''	726		725	722	5.019	3.894	tring(23), gCO(16), gCNO(15), bring(15), CC(6), bCOC(5)
32	Α"		694	696	692	5.626	5.807	tring(33), $\operatorname{bring}(25)$ , $\operatorname{gCO}(12)$ , $\operatorname{CC}(8)$
33	A''	635	07.	634	631	3.585	0.495	tring(54), gCl(26), gCH(6)
34	A'	000	597	599	596	8.102	1.641	bNO2r(25), bCO(19), bCCN(13), tring(8), CC(6), bCCl(5)
35	A'		0,7,1	566	563	12 179	4 379	hring(28) CN(14) Cl(8) hNO2sc(8) CC(8) gCO(8)
36	Δ"	504		506	502	7 129	1 772	tring(22), $cri(11)$ , $cr(0)$ , $br(22sc(0))$ , $cc(0)$ , $gcc(0)tring(22)$ $hring(17)$ $gCN(13)$ $Cr(10)$ $gCr(10)$ $hNO2r(5)$
37	Δ"	504	457	456	454	4 294	0.280	tring(53) gCN(10), gCl(9), gCH(6)
38	A'	412	-157	410	406	1 663	1.067	hCO(30) $hNO2r(25)$ tring(14) $hCCI(11)$
30	Δ"	412	320	328	324	2 292	4 684	tring(38) $bCOC(20)$ , $gCN(10)$ bring(6)
40	A'		52)	311	306	0.307	2 231	hring(32) $tring(16)$ $CN(13)$ $CI(0)$ $hCOC(7)$ $gCN(5)$
40	A A'		278	276	271	0.307 2.114	0.654	bCC(30) $bCO(21)$ $bCCN(14)$ $tCOm(11)$ $tOCH3(8)$
41	A		278	270	271	2.114	1.000	break(30), break(14), break(14), teoh(11), toeris(8), bring(7)
42	A''		100	261	258	0.427	1.288	gCN(41), gCl(16), tring(14), bCOC(6), gCH(6), gCNO(5)
43	A'		198	199	196	3.420	0.946	bCCN(49), bCCl(31), CC(7), bNO2r(6)
44	A''			169	164	0.101	0.362	tOCH3(73), bCO(9)
45	A''		142	139	137	2.515	3.078	tring(20), gCO(20), bCOC(18), gCH(12), tCOm(9), gCl(7)
46	A''			125	121	4.351	0.728	tCOm(70), tring(8), bCOC(6)
47	A''		90	88	83	3.203	1.459	tring(30), tNO(21), tCOm(20), gCN(14), gCH(6)
48	A''			53	49	0.715	1.502	tCOm(41), tNO(29), bCO(12)

Abbreviations used: b, bending; g, wagging; t, torsion; s, strong; vs, very strong; w, weak; vw, very weak;

<sup>a</sup> Relative absorption intensities normalized with highest peak absorption <sup>b</sup>Relative Raman intensities calculated by Eq 1 and normalized to 100. <sup>c</sup> For the notations used see Table-4.

reduction in frequencies of these modes compared to 5C2NA are due to the changes in the force constant, follow-on mainly from addition of 5C2NA and from different extents of mixing between the ring and substituent group's vibration.

**C-O vibrations:** The bands observed at 1527, 1526, 1523, 1440, 1438 and 1436 cm<sup>-1</sup> in C-O stretching vibrations for the 5C2NA compound. This mode can be described as vibrations, involving main contributions from the C-O stretching vibrations

[13]. The C-O out-of-plane vibration has an important contribution shown in Table-5. These modes are strongly coupled with ring torsion modes also.

**C-N vibrations:** The C-N vibrations is very difficult assignment, since mixing of several bands are possible in this region. In the present work, the strong band at 1106, 1105, 1102 cm<sup>-1</sup> and 1132, 1130, 1127 cm<sup>-1</sup> in FT-IR and FT-Raman spectrum have been assigned to C-N stretching vibrations.

**C-Cl vibrations:** In present study, The C-Cl stretching frequency is usually observed in the region 800-550 cm<sup>-1</sup> depending on the configuration and conformation of the compound [14]. Based on this, the FT-IR and Raman bands observed at 635, 634, 631, 506, 504, 502 cm<sup>-1</sup> and 599, 597, 596 have been assigned to C-Cl stretching modes show strong mixing with several planar modes. However, the planar C-Cl bending modes appear to be comparatively pure modes. The C-Cl out of plane bending modes were identified at 412, 410, 406 cm<sup>-1</sup> and 457, 456, 454 cm<sup>-1</sup> for IR and Raman, correspondingly.

**NO<sub>2</sub> vibrations:** The asymmetric stretching vibrations of NO<sub>2</sub> usually give rise to bands in the regions 1680-1450 cm<sup>-1</sup> in nitro groups [15], correspondingly. The symmetric stretching vibration match to Raman band at 1612, 1610, 1607 cm<sup>-1</sup> and the band at 1636, 1634, 1630 cm<sup>-1</sup> in FT-IR corresponds to NO<sub>2</sub> symmetric stretching vibrations. The deformation vibrations of NO<sub>2</sub> group (rocking, wagging and twisting) contribute to several normal modes in the low frequency region [16]. The strong band observed at 506, 504 and 502 cm<sup>-1</sup> in FT-IR spectrum correspond to NO<sub>2</sub> rocking vibration of the title compound. It should be highlighted that the wave number for the NO<sub>2</sub> rocking mode at 412, 410 and 406 cm<sup>-1</sup> is in good agreement with the corresponding experimental data.

Methyl group vibrations: For the assignments of CH<sub>3</sub> group frequencies, one can expect that nine basics can be connected to each CH<sub>3</sub> group, namely the symmetrical (CH<sub>3</sub> ips) and asymmetrical (CH3 ops), in-plane stretching modes (i.e. in-plane hydrogen stretching mode); the symmetrical (CH<sub>3</sub> ss) and asymmetrical (CH<sub>3</sub> ips), deformation modes; the inplane rocking (CH<sub>3</sub> ipr) out-of-plane rocking (CH<sub>3</sub> opr) and twisting (t CH<sub>3</sub>) bending modes. In addition to that, the asymmetric stretching (CH<sub>3</sub> ops) and asymmetric deformation (CH<sub>3</sub> opb) modes of the CH<sub>3</sub> group are expected to be depolarized for A" symmetry species [17]. The CH<sub>3</sub> ss stretching vibrations are observed at 3050, 3049 and 3046 cm<sup>-1</sup> in FT-IR frequencies. The Raman band observed at 3179, 3177 and 3176 cm<sup>-1</sup> in CH<sub>3</sub> ips and CH<sub>3</sub> ops stretching vibrations. In accordance with the CH<sub>3</sub> sb and CH<sub>3</sub> ipb vibrations in 5C2NA has been recognized at 1527, 1526, 1523 cm<sup>-1</sup> and 1539, 1536 and 1534 cm<sup>-1</sup> by B3LYP/6-311+G\*\* method. The theoretically calculated CH3 out-of-plane and in-plane bending modes have been found the recorded spectral values.

**Computed IR intensity and Raman activity analysis:** Computed vibrational spectral IR intensities and Raman behaviour of the corresponding wave numbers by B3LYP/6-311+G\*\* basis set have been obtained in the Table-6. Comparison of the IR intensities and Raman activities calculated by B3LYP/6-311+G\*\* level with experimental values exposes the variation of IR intensities and Raman activities.

TABLE-6
CALCULATED FORCE CONSTANT, IR INTENSITY
AND RAMAN ACTIVITY USING DFT METHOD
EOD THE 5CONA MOLECHIE

Reduced masses	Force constants	IR intensity	Raman activity
8.0234	0.0112	0.7770	1.5029
7.7628	0.0312	3.1237	1.4463
3.6201	0.0316	4.2339	0.7997
3.3601	0.0374	2.7053	3.0333
1.1035	0.0176	0.1009	0.3599
11.5901	0.2613	3.2721	0.8469
7.0112	0.2748	0.5345	1.2705
7.9378	0.3423	2.4490	0.7641
10.2488	0.5649	0.3195	2.1728
5.6043	0.3468	2.2889	4.8204
7.2107	0.7012	1.5922	0.9829
3.9621	0.4805	4.1243	0.2608
6.5954	0.9795	7.3250	1.9270
7.6456	1.4299	12.9492	4.0428
5.6240	1.1759	7.3033	1.8405
5.1836	1.2143	3.7207	0.5953
6.0351	1.7039	4.9032	5.8438
5.8728	1.8021	4.6327	3.6617
3.5225	1.2327	17.1783	1.5868
3.3577	1.3972	11.7453	7.6663
2.3389	0.9892	16.9860	5.3272
1.7274	0.8010	20.0867	1.6578
4.2501	2.0308	84.7004	1.5678
1.3145	0.7282	1.3184	0.9140
6.9280	4.4300	110.9511	12.4449
3.0728	2.1975	63.4152	34.3674
2.2157	1.6571	6.6082	5.4760
1.2502	1.0199	8.3333	1.3673
1.5435	1.2731	6.4690	5.6091
1.3880	1.2097	6.1836	7.3352
1.4686	1.4048	0.7913	5.5364
4.3013	4.1381	48.3190	146.8262
6.3880	6.8624	4.2960	1.4444
10.6252	12.2543	264.5182	175.4689
3.3957	4.1266	67.8199	14.8900
1.4562	1.9052	30.5681	5.3457
1.0647	1.4385	4.7263	19.7115
2.0755	2.8353	50.8872	4.8254
1.0520	1.4586	11.0065	14.5235
8.4632	12.8802	44.9772	26.3548
7.1813	11.2425	129.7758	69.6915
9.5151	15.4852	263.7583	15.1585
1.0379	5.6751	49.6413	84.2909
1.0981	6.3476	22.9695	49.2481
1.1057	6.5709	18.0138	103.5614
1.0897	6.7176	0.4370	55.4345
1.0919	6.7377	0.2492	57.4835
1.0943	6.8052	1.1965	115.8226

**Vibrational force constant:** The output files of the quantum mechanical calculations contain the force constant matrix in Cartesian coordinates and in Hartree/Bohr<sup>2</sup> units. These force constants were transformed to the force fields in the internal local-symmetry coordinates. The force field determined was used to calculate the vibrational potential energy distribution among the normal coordinate. They are listed in Table-6.

**First-order hyperpolarizability calculations:** The first-order hyperpolarizibility ( $\beta_{ijk}$ ) of the new molecular system of 5C2NA is calculated using B3LYP/6-311+G\*\* basis set

based on finite field approach. Hyperpolarizibility is a third rank tensor that can be described by a  $3 \times 3 \times 3$  matrix. It strongly depends on the method and basis set used. The 27 components of 3D matrix can be reduced to 10 components due to Kleinman [18] symmetry. The calculated first-order hyperpolarizability ( $\beta_{total}$ ) of 5C2NA is 6.0493 × 10<sup>-30</sup> esu, which is greater than that of urea  $(0.1947 \times 10^{-30} \text{ esu})$ . The calculated dipole moment ( $\mu$ ) and first-order hyperpolarizibility ( $\beta$ ) are shown in Table-7. The theoretical calculation looks to be more supportive in determination of particular compounds of  $\beta$  tensor than in establishing the real values of  $\beta$ . Domination of particular components indicates on a significant delocalization of charges in those directions. It is noticed that in  $\beta_{xyz}$ (which is the principal dipole moment axis and it is parallel to the charge transfer axis) direction, the biggest values of hyperpolarizability are noticed and subsequently delocalization of electron cloud is more in that direction. The higher dipole moment values are related, in general, with even larger projection of  $\beta_{total}$  quantities. The electric dipoles may enhance, oppose or at least bring the dipoles out of the required net alignment necessary for NLO properties such as  $\beta_{total}$  values. The connection between the electric dipole moments of an organic molecule having donor-acceptor substituent and first-

TABLE-7						
DIPOLE MOMENT	DIPOLE MOMENT AND FIRST-ORDER					
DERIVED FROM D	ET CALCULATIONS					
DERIVEDTROMD	TT CALCULATIONS					
$\beta_{xxx}$	-3.6266					
$\beta_{xxy}$	-5974.3					
$\beta_{xyy}$	-14.055					
$\beta_{yyy}$	30.154					
$\beta_{zxx}$	2.9637					
$\beta_{xyz}$	277.61					
$\beta_{zyy}$	-19.737					
$\beta_{xzz}$	-1.2935					
$\beta_{yzz}$	22.602					
β <sub>zzz</sub>	50.65					
$\beta_{\text{total}}$	6.0493					
μ <sub>x</sub>	0.65112166					
μ <sub>v</sub>	0.30784110					
μ <sub>z</sub>	0.52853045					
μ	1.21962831					
	20					

Dipole moment ( $\mu$ ) in Debye, hyperpolarizibility  $\beta(-2\omega;\omega,\omega) \ 10^{-30}$  esu.

order hyperpolarizability is widely recognized in the literature [19]. The maximum  $\beta$  was due to the behaviour of non-zero  $\mu$  value. One of the conclusions obtained from this work is that non-zero  $\mu$  value may enable the finding of a non-zero  $\beta$  value. Of course Hartee-Fock calculations depend on the mathematical method and basis set used for a polyatomic molecule.

Fig. 4 showed the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of 5C2NA. There is an opposite relationship between hyperpolarizability and HOMO-LUMO.

HOMO energy = -0.016 a.u LUMO energy = 0.009 a.u

## HOMO-LUMO energy gap = 0.025 a.u

**Electronic excitation mechanism:** The static polarizability value [20,21] is proportional to the optical strength and inversely proportional to the cube of transition energy. With this concept, larger oscillator strength ( $f_n$ ) and  $\Delta \mu_{gn}$  with lower transition energy ( $E_{gn}$ ) is favourable to obtain large first static polarizability values. Electronic excitation energies, oscillator strength and nature of the respective excited states were calculated by the closed-shell singlet calculation method and are summarized in Table-8. Representation of the orbital involved in the electronic transition was shown in Fig. 5.

TABLE-8				
COMPUTED ABSORPTION WAVELENGTH ( $\lambda_{ng}$ ),				
ENERGY (E.,), OSCILLATOR STRENGTH (f.)				
AND ITS MAJOR CONTRIBUTION				
n	$\lambda_{ng}$	$E_{ng}$	$f_n$	Major contribution
1	342.6	29.2	0.0001	H-2->L+0(+25 %), H-4->L+0(22 %)
2	293.4	34.1	0.0001	H-4->L+0(+37 %), H-4->L+2(+21 %)
3	179.7	55.7	0.1208	H-0->L+0(+75 %)
(Assignment; H=HOMO, L=LUMO, L+1=LUMO+1, etc.)				

#### Conclusion

The geometry of 5C2NA has been optimized using B3LYP/ 6-311+G\*\* basis sets. The bond length, bond angle and dihedral angles were established and tabulated. The experimental IR and Raman vibrational frequencies agree well with the computed values after proper scaling done. The vibrational wave numbers, IR and Raman activities are calculated and they were found in



Fig. 4. Representation of the orbital involved in the electronic transition for (a) HOMO (b) LUMO (c) Virtual



understood by examining the energetic of frontier molecular orbitals. There is an opposite relationship between hyperpolari-

zability and HOMO-LUMO.

very good agreement. By using B3LYP/6-311+G\*\* the firstorder hyperpolarizibility ( $\beta_{ijk}$ ) of the novel molecular system of 5C2NA is calculated the basis set based on finite field approach. 6.0493 × 10<sup>-30</sup> esu was found by the calculation of the first-order hyperpolarizability ( $\beta_{total}$ ) of 5C2NA which is greater than that of urea (0.1947 × 10<sup>-30</sup> esu). The anisotropy polarizability invariant is computed with the numerical derivative of the dipole moment using B3LYP/6-311+G\*\*. Electronic excitation energies, oscillator strength and character of the respective excited states were calculated by the closedshell singlet calculation method. The NLO responses can be

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Fig. 5. Representation of the orbital involved in the electronic transition for (a) HOMO-0 (b) LUMO+0 (c) HOMO-2 (d) HOMO-4 (e) LUMO+2