Available online at www.elixirpublishers.com (Elixir International Journal)



Contract St.



Elixir Vib. Spec. 91 (2016) 38087-38098

# **Slizciv** ISSN: 2229-712X

# FT-IR, FT-RAMAN, NMR Spectral analysis and theoretical NBO, HUMO-LUMO analysis of 3,5-dimethylpiperidine by *ab initio* HF and density functional methods

K.Sambathkumar<sup>a</sup> & K.Settu<sup>a</sup>

<sup>a</sup>P.G.&Research Department of Physics, A.A.Govt.Arts College, Villupuram-605602.India.

ARTICLE INFO Article history: Received: 10 December 2015; Received in revised form: 28 January 2016; Accepted: 3 February2016;

Keywords FT-IR, FTt-Raman, Homo- Lumo, NBO, NMR, DMP

## ABSTRACT

The Fourier-transform infrared spectrum of 3, 5-dimethylpiperidine (DMP) was recorded in the region 4000-400cm<sup>-1</sup>. The Fourier-transform Raman spectrum of DMP was also recorded in the region 3500-50 cm<sup>-1</sup>. Quantum chemical calculations of energies, geometrical structure and vibrational wavenumbers of DMP were carried out ab initio HF and density functional theory (DFT/B3LYP) method with 6-31+G (d,p) basis set. The difference between the observed and scaled wavenumber values of most of the fundamentals is very small. The values of the total dipole moment ( $\mu$ ) and the first-order hyperpolarizability( $\beta$ ) of the investigated compound were computed using *ab initio* quantum mechanical calculations. The calculated results also show that the DMP might have microscopic nonlinear optical (NLO) behavior with non-zero values. The difference between the observed and scaled wave number values of most of the fundamentals is very small. A detailed interpretation of the FT-IR, FT-Raman, NMR spectra of DMP was also reported. Natural bond orbital analysis has been carried out to explain the charge transfer or delocalization of charge due to the intra-molecular interactions. Energy of the highest occupied molecular (HOMO) orbital and lowest unoccupied (LUMO) molecular orbital have been predicted. Temperature dependence of various thermodynamic properties like heat capacity, enthalpy, Gibb's free energy, entropy is increase with increase in temperature.

### © 2016 Elixir all rights reserved.

## Introduction

Piperidines are an important group of heterocyclic compounds in the field of medicinal chemistry owing to the fact that these can frequently be recognized in the structure of numerous naturally occurring alkaloid and synthetic compounds with interesting biological and pharmacological properties. Piperidine derivatives were also reported to posses analgesic [1,2] anti-inflammatory [2] central nervous system [3-7] local anesthetic [3-8] anticancer [9] and antimicrobial activity [10]. Piperidine nucleus is also found in drugs as raloxifene, minaxidil [11] and as a raw material for preparing epoxy resins, corrosion inhibitors and autioxidant [12]. The vibrational studies of piperidine on theoretical studies of density functional calculations were also reported [13-20]. To our knowledge, literature survey also reveals that to the best of our knowledge no theoretical calculations or detailed vibrational infrared and Raman analysis have been performed on 3,5-dimethylpiperidine (DMP) molecule so far.

A systematic study on the vibrational spectra and structure will aid in understanding the vibrational modes of this title molecule. So, in this study, the vibrational wave numbers, geometrical parameters, modes of vibrations, minimum energy, NMR and electrostatic potential also provide information about electronic effects of DMP molecule were investigated by using ab initio HF and DFT/B3LYP methods with 6-31+G(d,p) basis set. Specific scale factors were also used and employed in the predicted frequencies. The electronic dipole moment ( $\mu$ ) and the first

hyperpolarizability ( $\beta$ ) value of the investigate molecule computed show that the DMP molecule might have microscopic nonlinear optical (NLO) behavior with non-zero values. The calculated HOMO and LUMO energies show that charge transfer occurs in the molecule. Moreover, Natural bond orbital analysis (NBO) performed using NBO 3.1 program provides valuable information about various intermolecular interactions that are responsible for its bioactivity.

## **Experimental Details**

The fine sample of DMP was purchased from Lancaster chemical company, UK and it was used as such without any further purification to record FTIR and FT-Raman spectra. The FTIR spectra of title compound was recorded in the region 4000-400 cm<sup>-1</sup> at a resolution of  $\pm 1$  cm<sup>-1</sup> using BRUKER IFS 66V model FTIR spectrometer equipped with an MCT detector, a KBr beam splitter and globar source. The FT-Raman spectrum of DMP was recorded using 1064 nm line of Nd: YAG laser as excitation wavelength in Strokes region (3500-50 cm<sup>-1</sup>) on a BRUKER IFS-66V model interferometer equipped with an FRA-106 FT-Raman accessory operating at 200 mWpower. The calibrated wave numbers are expected to be accurate within  $\pm cm^{-1}$ .

#### **Computational Details**

For meeting the requirements of both accuracy and computing economy, theoretical methods and basis sets should be considered. DFT has proved to be extremely useful in treating electronic structure of molecules. The HF and DFT calculations were carried out for DMP with GAUSSIAN 09W program package [21]. Initial geometry generated from the standard geometrical parameters was minimized without any constraint on the potential energy surface at Hartree-Fock level adopting the standard 6-31+G (d,p) basis set. This geometry was then re-optimized again at DFT level employing the B3LYP keyword, which invokes Becke's three-parameter hybrid method [22] using the correlation function of Lee et al.[23], implemented with the same basis set for better description of the bonding properties of NH group. All the parameters were allowed to relax and all the calculations converged to an optimized geometry which corresponds to a true minimum, as revealed by the lack of imaginary values in the wave number calculations. The Cartesian representation of the theoretical force constants have been computed at the fully optimized geometry.

The multiple scaling of the force constants were performed according to SQM procedure [24] using selective scaling in the natural internal coordinate representation [25]. Transformation of force field, the subsequent normal coordinate analysis including the least square refinement of the scale factors and calculation of the total energy distribution (TED) were done on a PC with the MOLVIB program (version V7.0-G77) written by Sundius [26,27]. The systematic comparison of the results from DFT theory with results of experiments has shown that the method using B3LYP functional is the most promising in providing correct vibrational wave numbers. The calculated geometrical parameters were compared with X-ray diffraction result [28]. Normal coordinate analyses were carried out for the title compound to provide a complete assignment of fundamental frequencies. For this purpose, the full set of 62 standard internal coordinates (containing 14 redundancies) for DMP was defined as given in Table 1. 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. [25] is summarized in Table 2. The theoretically calculated force fields were transformed to this set of vibrational coordinates and used in all subsequent calculations.

#### **Prediction of Raman intensities**

The Raman activities (Si) calculated with the GAUSSIAN 09W program were subsequently converted to relative Raman intensities (Ii) using the following relationship derived from the basic theory of Raman scattering [29],

No. (i)	Symbol	Туре	Definition <sup>a</sup>
Stretchin	g		
1 – 3	R <sub>i</sub>	С-Н	$C_2 - H_8, C_4 - H_{13}, C_8 - H_{18}$
4-9	r <sub>i</sub>	C-C	C <sub>2</sub> - C <sub>3</sub> , C <sub>3</sub> - C <sub>4</sub> , C <sub>4</sub> - C <sub>5</sub> , C <sub>5</sub> - C <sub>6</sub> , C <sub>3</sub> - C <sub>9</sub> , C <sub>5</sub> - C <sub>14</sub>
10	Si	N-H	N <sub>1</sub> - H <sub>7</sub>
11-12	$q_i$	N-C	$N_1-C_2, N_1-C_6$
13-18	P <sub>i</sub>	C-H <sub>3</sub> methyl	$C_9$ - $H_{10}$ , $C_{9}$ - $H_{11}$ , $C_{9}$ - $H_{12}$ , $C_{14}$ - $H_{15}$ , $C_{14}$ - $H_{16}$ , $C_{14}$ - $H_{17}$
In-plane	bending		
19 - 24	$\alpha_{i}$	Ring	$N_1 - C_2 - C_3, C_2 - C_3 - C_4, C_3 - C_4 - C_5,$ $C_4 - C_5 - C_6, C_5 - C_6 - N_1, C_6 - N_1 - C_2$
25 - 30	$\beta_i$	С-С-Н	$C_{3}\text{-}C_{4}\text{-}H_{13}, C_{5}\text{-}C_{4}\text{-}H_{13}, C_{5}\text{-}C_{6}\text{-}H_{18}, N_{1}\text{-}C_{6}\text{-}H_{18}, N_{1}\text{-}C_{2}\text{-}H_{8}, C_{3}\text{-}C_{2}\text{-}H_{8}$
31-36	$\lambda_i$	C-C-H methyl	$C_3-C_9-H_{12}, C_3-C_9-H_{11}, C_3-C_9-H_{10}, C_5-C_4-H_{17}, C_5-C_{14}-H_{15}, C_5-C_{14}-H_{16}$
37-42	pi	C-H-H methyl	$C_{9}-H_{11}-H_{10}, C_{9}-H_{11}-H_{12}, C_{9}-H_{12}-H_{10}, C_{14}-H_{16}-H_{15}, C_{14}-C_{16}-H_{17}, C_{14}-H_{15}-H_{17}$
43-46	$\mathbf{Z}_{\mathbf{i}}$	C-C-C	C <sub>2</sub> - C <sub>3</sub> - C <sub>9</sub> , C <sub>4</sub> - C <sub>3</sub> - C <sub>9</sub> , C <sub>4</sub> - C <sub>5</sub> - C <sub>14</sub> , C <sub>6</sub> - C <sub>5</sub> - C <sub>14</sub>
47-48	X <sub>i</sub>	C-N-H	C <sub>2</sub> -N <sub>1</sub> - H <sub>7</sub> , C <sub>6</sub> - N <sub>1</sub> -H <sub>7</sub>
Out-of-p	lane bendin	ıg	
49-51	$\psi_{i}$	C-H	$H_8 - C_2 - N_1 - C_3, H_{13} - C_4 - C_3 - C_5, H_{18} - C_6 - C_5 - N_1$
52	$\rho_{i}$	N-H	$H_7 - N_1 - C_2 - C_6$
53,54	χi	C-C	$C_9 - C_3 - C_4 - C_2, C_{12} - C_5 - C_4 - C_6$
Torsion			
55 - 60	τ	t Ring	$N_1 - C_2 - C_3 - C_4, C_2 - C_3 - C_4 - C_5, C_3 - C_4 - C_5 - C_6, C_4 - C_5 - C_6 - N_1, C_5 - C_6 - N_1 - C_2, C_6 - N_1 - C_2 - C_3$
61	τ	t C-CH <sub>3</sub>	$(C_6, C_4)$ - $C_5$ - $C_{12}$ - $(H_{15}, H_{16}, H_{17})$
62	$\tau_i$	t C-CH <sub>3</sub>	$(C_2, C_4)- C_3 - C_9 - (H_9, H_{10}, H_{11})$

 Table 1.Definition of internal coordinates of 3,5- Dimethylpiperidine.

<sup>a</sup>For numbering of atoms refer Fig.1

No. (i)	Туре	Definition	HF/6-31G+(d,p)	B3LYP/6-31G+(d,p)
1-3	СН	$R_1, R_2, R_3$	0.910	0.974
4-9	CC	r <sub>4</sub> ,r <sub>5</sub> ,r <sub>6</sub> ,r <sub>7</sub> ,r <sub>8</sub> ,r <sub>9</sub>	0.901	0.954
10	NH	S <sub>10</sub>	0.951	1.001
11,12	NC	$q_{11}, q_{12}$	0.910	0.989
13,14	CH <sub>3</sub> ss	$(p_{13} + p_{14} + p_{15}) / \sqrt{3}$ , $(p_{16} + p_{17} + p_{18}) / \sqrt{3}$	0.910	0.991
15-16	CH <sub>3</sub> ass	$(2p_{13} + p_{14} + p_{15}) / \sqrt{6}, (2p_{16} + p_{17} + p_{18}) / \sqrt{6}$	0.899	0.971
17-18	CH <sub>3</sub> ops	$(p_{14} - p_{15}) / \sqrt{6} , (p_{17} - p_{18}) / \sqrt{6}$	0.920	0.990
19	R trigd	$(\alpha_{19} - \alpha_{20} + \alpha_{21} - \alpha_{22} + \alpha_{23} - \alpha_{24}) / \sqrt{6}$	0.960	0.990
20	R symd	$(-\alpha_{19} - \alpha_{20} + 2\alpha_{21} - \alpha_{22} - \alpha_{23} + 2\alpha_{24}) / \sqrt{12}$	0.930	0.990
21	R asymd	$(\alpha_{19} - \alpha_{20} + \alpha_{22} - \alpha_{23}) / \sqrt{2}$	0.891	0.990
22-24	b C H	$(\beta_{25} - \beta_{26}) / \sqrt{2}, (\beta_{27} - \beta_{28}) / \sqrt{2}, (\beta_{29} - \beta_{30}) / \sqrt{2}$	0.961	0.911
25,26	CH <sub>3</sub> sb	$(-\lambda_{31} - \lambda_{32} - \lambda_{33} + \lambda_{34} + \lambda_{35} + \lambda_{36})/\sqrt{2}$	0.961	1.005
		$(-p_{37}-p_{38}-p_{39}+p_{40}+p_{41}+p_{42})/\sqrt{2}$		
27,28	CH <sub>3</sub> ipb	$(2 \lambda_{34} - \lambda_{35} - \lambda_{36})/\sqrt{6}$ , $(2 p_{40} - p_{41} - p_{42})/\sqrt{6}$	1.000	0.931
29,30	$CH_3  opb$	$(-\lambda_{34} + \lambda_{35})/\sqrt{2} (-p_{40} + p_{41})/\sqrt{2}$	0.891	0.971
31,32	CH <sub>3</sub> ipr	$(-\lambda_{31}-\lambda_{32}+2\lambda_{33})/\sqrt{6},(-p_{37}-p_{38}+2p_{39})/\sqrt{6}$	0.915	0.911
33,34	CH <sub>3</sub> opr	$(-\lambda_{32}+\lambda_{33})/\sqrt{2}, (-p_{38}+p_{39})/\sqrt{2}$	0.923	0.901
35,36	b C C	$(Z_{43} - Z_{44}) / \sqrt{2}, (Z_{45} - Z_{46}) / \sqrt{2}$	0.911	0.910
37	b N H	$(X_{47} - X_{48}) / \sqrt{2}$	0.920	0.901
38-40	ωCΗ	$\psi_{49}, \psi_{50}, \psi_{51}$	0.931	0.910
41	ωNH	ρ <sub>52</sub>	0.920	0.910
42,43	ωCC	X 53 .X 54	0.900	0.901
44	Ring trigd	$(\tau_{55} - \tau_{56} + \tau_{57} - \tau_{58} + \tau_{59} - \tau_{60}) / \sqrt{6}$	0.911	0.990
45	Ring symd	$(\tau_{55} - \tau_{56} + \tau_{58} - \tau_{59}) / \sqrt{2}$	0.911	0.990
46	Ring asymd	$(-\tau_{55} + 2\tau_{56} - \tau_{57} - \tau_{58} + 2\tau_{59} - \tau_{60}) / \sqrt{2}$	0.911	0.990
47,48	t C-CH <sub>3</sub>	$\tau_{61}, \tau_{62}$	0.911	0.990

Table 2.	Definition	of Local S	Symmetry	Coordinates	of 3.5-	Dimethy	vlnii	peridine
1 4010 -	Dermittion	OI LOUGH L	y manade of y	COOL WITHERCO	01 0 40	D IIII CUII	/	JOI IGHING

<sup>a</sup>The internal coordinates used here are defined in Table1

$$I_i = \frac{f(v_0 - v_i)^4 Si}{v_i \left[1 - \exp\frac{-hcv_i}{kT}\right]}$$

Where v0 is the exciting frequency in  $\text{cm}^{-1}$ , vi the vibrational wave number of the ith normal mode, h, c and k are the fundamental constants and f is a suitably chosen common normalization factor for all the peak intensities.

#### **Results and Discussion Molecular Geometry**

The optimized molecular structure of DMP along with numbering of atoms is shown in Fig. 1. The optimized geometrical parameters of DMP obtained by DFT-B3LYP/6-31+G(d,p) and HF/6-31+G(d,p) levels are listed in Table 3. From the structural data given in Table 3, it is observed that the various bond lengths are found to be almost same at HF/6-31+G(d,p) and B3LYP/6-31+G (d,p) levels. However, the B3LYP/6-31+G(d,p) level of theory, in general slightly over estimates bond lengths but it yields bond angles in excellent agreement with the HF method. The calculated geometric parameters can be used as foundation to calculate the other parameters for the compound.



Fig 1. Molecular structure of 3,5-Dimethylpiperidine

Bond length	Valu	e (Å)	v		Valu		
_	HF/	B3LVP/ Exn <sup>a</sup>		Bond angle	HF/	B3LYP/	Exp <sup>a</sup>
	6-31G+(d,p)	6-31G+(d,p)	r		6-31G+(d,p)	6-31G+(d,p)	r
N1-C 2	1.3999	1.3979		C5-C14-H15	110.96	110.88	
N1-C6	1.3999	1.3979		C5-C14-H16	111.43	111.81	
N1-H7	0.9944	1.0073		C5-C14-H17	110.92	110.06	
C2-C3	1.3673	1.0832	1.510(2)	H15-C14-H16	107.95	108.04	121.98 (17)
C3-C4	1.4232	1.4269	1.518 (2)	H15-C14-H17	107.53	107.06	
C3-C9	1.5088	1.5085		H16-C14-H17	107.86	107.97	119.46 (18)
C4-C5	1.4232	1.4269	1.5506 (19)	Dihedral angle(°)			
C4-H13	1.0763	1.0854	1.523 (2)	C6-N1-C2-C3	9.0505	4.268	
C5-C6	1.3673	1.37		C6-N1-C2-H8	-174.418	-177.46	
C2-H8	1.073	1.083		H7-N1-C2-C3	154.97	170.03	
C5-C14	1.5088	1.5085	1.520(2)	H7-N1-C-H8	-28.489	-11.70	
C6-H18	1 0733	1 0832		C2-N1-C6-C5	-9 0498	-4 268	
C9-H10	1.0755	1.0052	1 370 (3)	C2-N1-C6-H18	174.42	177.46	
C9-1110	1.0805	1.0908	1.370 (3)	U7 N1 C6 C5	174.42	177.40	
С9-ПП	1.0803	1.097		H7-N1-C0-C3	-134.97	-170.05	
C9-H12	1.0845	1.0942		H/-NI-C6-HI8	28.494	11./01	50.00 (1.0)
C14-H15	1.0863	1.0968		NI-C2-C3-C4	-3.6/1	-1.657	-58.03 (14)
C14-H16	1.0845	1.0942		N1-C2-C3-C9)	176.40	178.37	
C14-H17	1.0865	1.097		H8-C2-C3-C4	-179.94	-179.78	
Bond angle(°)				H8-C2-C3-C9	0.1303	0.2465	
C2-N1-C6	118.752	120.583	113.75 (11)	C2-C3-C4-C5	-1.8467	-0.908	37.74 (17)
C2-N1-H7	116.121	118.945		C2-C3-C4-H13	-179.80	-179.66	
C6-N1-H7	116.120	118.94		C9-C3-C4-C5	178.07	179.05	
N1-C2-C3	121.425	120.436		C9-C3-C4-H13)	0.1164	0.304	
N1-C2-H8	115.62	116.066		C2-C3-C9-H10	122.17	121.29	
С3-С2-Н8	122.84	123.473		C2-C3-C9-H11	-118.36	-119.91	
C2-C3-C4	118.969	119.409	117.08 (12)	C2-C3-C9-H12	1.836	0.639	
C2-C3-C9	120.83	120.40		C4-C3-C9-H10	-57.747	-58.67	
C4-C3-C9	120.199	120.19		C4-C3-C9-H11	61.719	60.121	
C3-C4-C5	119.80	119.60	111.98 (11)	C4-C3-C9-H12	-178.08	-179.32	
C3-C4-H13	120.08	120.19	111.32 (13)	C3-C4-C5-C6	1.8475	0.908	
C5-C4-H13	120.08	120.19	112.70 (13)	C3-C4-C5-C14	-178.05	-179.05	-171.04 (11)
C4-C5-C6	118.97	119.40		C13-C4-C5-C6	179.80	179.66	
C4-C5-C14	120.20	120.19	110.19 (11)	C13-C4-C5-C14	-0.0977	-0.304	
C6-C5-H14	120.82	120.40		C4-C5-C6-N1	3.669	1.656	2.17 (16)
N1-C6-C5	121.43	120.43		C4-C5-C6-H18	179.94	179.788	
N1-C6-H18	115.62	116.06		C14-C5-C6-N1	-179.42	-178.37	
C5-C6-H18	122.84	123.47		C14-C5-C6-H18	-0.1552	-0.2469	
C3-C9-H10	110.96	110.88		C4-C5-C14-H15	57.839	58.687	
C3-C9-H11	110.92	110.86		C4-C5-C14-H16	178,1745	179.34	
C3-C9-H12	111.0.02	111.80		C4-C5-C14-H17	-61 627	-60 1075	
H10-C9-H11	107.53	107.06		C6-C5-C14-H15	-122.06	-121 7	
H10-C9H12	107.95	107.00		C6-C5-C14-H16	-1 727	-0.6244	
Н11_С0_Н12	107.95	107.07		C6 C5-C14-H17	118 /6	110 07	
1111-09-1112	107.00	107.77		0005-014-1117	110.40	117.74	

# Table 3. Optimized geometrical parameters of 3, 5- Dimethylpiperidine obtained by B3LYP/6-31+G (d,p) and HF/6-31G+(d,p) density functional theory calculations.

For numbering of atoms refer Fig. 1.

<sup>a</sup>Experimental values are taken from Ref.[28].

The optimized molecular structure of DMP reveals that the two methyl groups are in planar with the heterocyclic ring. Inclusion of CH<sub>3</sub> group and NH atoms known for its strong electron-with drawing nature. It is expected to increase a contribution of the resonance structure, in which the electronic charge is concentrated at this site. This is the reason for the shortening of bond lengths C9-H10=1.0863A<sup>0</sup>, C9-H11= 1.0865A<sup>0</sup>, C9-H12=1.0845A<sup>0</sup>, C14-H15=1.0863A<sup>0</sup>, C14-H16=1.0845A<sup>0</sup> and C14-H17=1.0865A<sup>0</sup> and obtained by HF method. The same bond lengths calculated by DFT method is found to be 1.0968, 1.097, 1.0942, 1.0968, 1.0942 and 1.097A<sup>0</sup>. The carbon atoms are bonded to the hydrogen atoms with an  $\sigma$ -bond in heterocyclic ring and the substitution of CH<sub>3</sub> atoms for hydrogen reduces the electron density at the ring carbon atom. In DMP, the N-H bond lengths vary from  $0.9944A^{\circ}$  to  $1.0073A^{\circ}$  respectively, by HF and B3LYP methods. The carbon atoms in substituted to heterocyclic ring exert a larger attraction on the valence electron cloud of the hydrogen atom resulting in an increase in the CH3 force constants and a decrease in the corresponding bond length.

It is evident from the C-C bond lengths ranging from 1.3673  $A^0$  to 1.5088  $A^0$  by HF method and from 1.0832 to 1.5085 by B3LYP method in the heterocyclic ring of DMP, whereas the C-H bond lengths in DMP vary from 1.073 $A^0$  to 1.0763 $A^0$  and from 1.083 $A^0$  to 1.0854 $A^0$  by HF and B3LYP methods, respectively. The heterocyclic ring appears to be a little distorted because of the CH<sub>3</sub> group substitution as seen from the bond angles C2-C3-C4, C4-C5-C6 which are calculated as 118.969°, 118.97° and 119.409°, 119.40° respectively, by HF and B3LYP methods and are larger than typical hexagonal angle of 120°.

#### First Hyperpolarizability

The potential application of the title compound in the field of nonlinear optics demands, the investigation of its structural and bonding features contribution to the hyperpolarizability enhancement, by analysing the vibrational modes using IR and Raman spectroscopy. Many organic molecules, containing conjugated  $\pi$  electrons are characterized by large values of molecular first hyper polarizabilities, were analysed by means of vibration spectroscopy [30]. In most of the cases, even in the absence of inversion symmetry, the strongest band in the Raman spectrum is weak in the IR spectrum and vice-versa. But the intramolecular charge from the donor to acceptor group through a  $\pi$ -bond conjugated path can induce large variations of both the molecular dipole moment and the molecular polarizability, making IR and Raman activity strong at the same time. The experimental spectroscopic behavior described above is well accounted for a calculations in  $\pi$ conjugated systems that predict exceptionally infrared intensities for the same normal modes. The first hyperpolarizability ( $\beta$ ) of this novel molecular system is calculated using the abinitio quantum mechanical method, based on the finite-field approach. In the presence of an applied electric field, the energy of a system is a function of the electric field. The first hyperpolarizability is a third-rank tensor that can be described by a 3x3x3 matrix.

The 27 components of the 3D matrix can be reduced to 10 components due to the Kleinman symmetry [31]. The components of  $\beta$  are defined as the coefficients in the Taylor series expansion of the energy in the external electric field. When the electrical field is weak and homogeneous, this expansion becomes

$$E = E_0 - \sum_{i} \mu_i F^i - \frac{1}{2} \sum_{ij} \alpha_{ij} F^i F^j - \frac{1}{6} \sum_{ijk} \beta_{ijk} F^i F^j F^k - \frac{1}{24} \sum_{ijkl} v_{ijkl} F^i F^j F^k F^l$$

Where  $E_0$  is the energy of the unperturbed molecule;  $F^1$  is the field at the origin; and  $\mu_i$ ,  $\alpha_{ij}$ ,  $\beta_{ijk}$  and  $\gamma_{ijkl}$  and are the components of dipole moment, polarizability, the first and second hyperpolarizibilities, hyperpolarizabilities respectively. The calculated total dipole moment  $(\mu)$  and mean first hyperpolarizability ( $\beta$ ) of DMP are 0.4112 Debye and 2.1749  $x10^{-30}$  esu, respectively, which is comparable with the reported values of similar derivatives. The large value of hyperpolarizibilities,  $\beta$  which is a measure of the non-linear optical activity of the molecular system, is associated with the intramolecular charge transfer, resulting from the electron cloud movement through  $\pi$  conjugated frame work from electron donor to electron acceptor groups. The physical properties of these conjugated molecules are governed by the high degree of electronic charge delocalization along the charge transfer axis and by the low band gaps. So we conclude that the title compound is an attractive object for future studies of nonlinear optical properties.

#### Natural Bond Orbital Analysis

NBO analysis provides the most accurate possible 'natural Lewis structure' picture of because all orbital details are mathematically chosen to include the highest possible percentage of the electron density. Interaction between both filled and virtual orbital spaces information correctly explained by NBO analysis, it could enhance the analysis of intra-inter-molecular interactions.

The second order Fock matrix was carried out to evaluate the donor (i)-acceptor (j) i.e donor level bonds to acceptor level bonds interactions in the NBO analysis [32].The interaction result is a loss of occupancy from the localized NBO of the idealized Lewis structure into an empty non-Lewis orbital. For each donor (i) and acceptor (j), the stabilization energy  $E^2$  associated with the delocalization  $i \rightarrow j$  is estimated as

$$E^{(2)} = \Delta E_{ij} = q_i \frac{F(i, j)^2}{\varepsilon_j - \varepsilon_i}$$

Where  $q_i$  is the donor orbital occupancy, are  $\varepsilon_i$  and  $\varepsilon_i$ diagonal elements and F (i,j) is the off diagonal NBO Fock matrix element. Natural bond orbital analysis provides an efficient method for studying intra and intermolecular bonding and interaction among bonds, and also provides a convenient basis for investigating charge transfer or conjugative interaction in molecular systems. Some electron donor orbital, acceptor orbital and the interacting stabilization energy resulted from the second-order micro-disturbance theory are reported [33, 34]. The large the  $E^{(2)}$  value the more intensive is the interaction between electron donors and electron acceptors, i.e., the more donating tendency from electron donors to electron acceptors and the greater the extent of conjugation of the whole system . Delocalization of electron density between occupied Lewis-type (bond or lone pair) NBO orbitals and formally unoccupied (antibond or Rydgberg) non-Lewis NBO orbitals correspond to a stabilizing donor-acceptor interaction. NBO analysis has been performed on the DMP molecule at the DFT/ B3LYP/ 6-31G+ (d,p) level in order to elucidate, the intra-molecular, rehydridization and delocalization of electron density within the molecule. Maximum energy transfer from lone pair nC(5)to  $\pi^*$ (N1-C6) (74.83 Kcal/mol), this investigation deeply

mentioned the energy delocalization from the lone pair of the molecule to other part, which is listed in Table 4. The intra molecular hyper conjugative interactions are formed by the orbital overlap between n(C) and  $\pi^*$ (N-C) bond orbital which results in ICT (intramolecular charge transfer) causing stabilization of the system.

 Table 4. Second order perturbation analysis of Fock

 matrix in NBO basis for 3.5- Dimethylpiperidine.

Donor(i)	ED/e	Acceptor(j)	ED/e	<sup>a</sup> E(2)	<sup>b</sup> E(j)-	°F(i,j)
					E(i)	
σC2-H8	0.99082	σ*(N1-C6)	0.00863	2.21	1.06	0.061
σ C4-H13	0.98978	σ*C2-C3)	0.01001	2.00	1.07	0.059
σ C4-H13		σ(C5-C6)	0.01001	2.00	1.07	0.059
σ C6-H18	0.99082	σ*(N1-C2)	0.00863	2.21	1.06	0.061
π N1-C6	0.99252	π* (C2-C3)	0.01001	12.18	0.36	0.086
π C2-C3	0.98802	n*(C4	0.00108	27.34	0.18	0.100
π C2-C3	0.81802	π* (N1-C6)	0.23632	6.86	0.23	0.052
nC5	0.99955	n*(C4)	0.00020	270.93	0.14	0.141
nC5		$\pi^{*}(N1-C6)$		74.83	0.09	0.121
nC5		σ*(C14-	0.00424	2.23	0.58	0.062
		H17)				
n*C4	0.39015	π*(C2-C3)	0.14123	34.65	0.10	0.100
π*N1-C6	0.23632	π*(C2-C3)		26.77	0.05	0.072

<sup>a</sup>E<sup>(2)</sup> means energy of hyperconjugative interactions (stabilization energy) <sup>b</sup>Energy difference between donor and acceptor i and j NBO orbitals. <sup>c</sup>F(ij) is the Fock matrix element between i and j NBO orbitals.

The n-  $\pi$  conjugation between the N and C lone pair electrons and hetero cyclic ring  $\pi$  system is strong in the ground state. The nC5 $\rightarrow \pi^*(N1-C6)$ , nC5 $\rightarrow \sigma^*(C14-H17)$ energies are 74.83 and 2.23 respectively shows n and  $\pi$ conjugation between nitrogen, carbon and hetero cyclic ring. In DMP  $\pi(N1-C6) \rightarrow \pi^*(C2-C3)$  interaction is seem to give a strong stabilization 12.18 Kcal/mol. This strong stabilization denotes the large delocalization. The interesting interactions in DMP molecule are  $nC5 \rightarrow n^*C4$  these interaction result the enormous stabilization energy of 270.93 Kcal/mol respectively. This highest interaction around the ring can induce the large bioactivity in the molecule. Hence the DMP structure is stabilized by these orbital interactions.

#### NMR Spectral Analysis

NMR Spectroscopy is a powerful technique that can provide detailed information on the topology, dynamics and three-dimensional structure of molecules in solid state and solution. This technique used to obtain physical, chemical, electronic and structural information about molecules due to their chemical shift, on the resonant frequencies of the nuclei present in the molecule. GIAO/DFT (Gauge including atomic orbital/density functional theory) approach is widely used as for the calculations of chemical shifts for different type of molecules [35-38]. 13C -NMR chemical shift is one of the important tools in determining the presence or absence of particular atom in a particular position of a molecular system. In a molecule, shielding of atom like carbon is greatly affected by neighboring bonded atoms and similar bonded atoms give different shielding values in different environments. Bv adopting the procedure recommended the chemical shift values for carbon atom have been studied. The NMR calculation were carried out at B3LYP/6-31+G (d,p) levels of theory in the gas phase. In this work the chemical shift ( $\delta$ ) for carbon atoms presented in the DMP in gas phase has been studied and theoretical 13C,1H-NMR isotropic shielding of carbon and Hydrogen atom and NMR shielding surface as shown in Fig 2.



# Fig 2. Prediction of 13C ,1H chemical shift value of [δ (ppm)] of 3,5-Dimethylpiperidine.

The 1H and 13C chemical shifts were measured in a less polar (CDCl<sub>3</sub>) solvent. The result in Table 5 shows that the range 13C NMR chemical shift of the typical organic molecule usually ensures reliable interpretation of spectroscopic parameters. It is true from the above literature value, in our present study, the title molecule DMP also falls with the above literature data except with the methyl carbon atoms. The result shows that the range 13C NMR chemical shifts of the typical organic molecule usually [39,40], the accuracy ensures reliable interpretation of spectroscopic parameters. It is true from the above literature value in our present study, that the title molecule DMP also shows that same. The molecule structure of the title molecule shows that the two CH<sub>3</sub> are present in two different positions. The presence of electronegative atom attracts all electron clouds of carbon atom towards the CH3 atom, which leads to deshielding of carbon atom and the net result is increase in chemical shift values. So the CH3 atoms show electronegative property (they attract the other atom towards), but the chemical shift of C<sub>2</sub>, C<sub>3</sub>, C<sub>4</sub>, seems to be (C<sub>2</sub>=82.907; C<sub>3</sub>= 54.917; C<sub>4</sub>=92.800 ppm) by B3LYP/6-31G+ (d,p) method same for other carbon atoms but in N1 the chemical shift is higher value i.e. 153.765 ppm using B3LYP/6-31G+(d,p) methods. The H atom is the smallest of all atoms and mostly localized on the periphery of molecules. Therefore their chemical shifts would be more susceptible to intermolecular interactions in the aqueous solution as compared to that for other heavier atoms. The  $H_8$ ,  $H_{13}$  and  $H_{18}$  are expected to give rise to NMR signals in (27.1-28.5) ppm range. Another important aspect is that, hydrogen attached or nearly electronwithdrawing atom or group can decrease the shielding and more the resonance of attached proton towards to a higher frequency. By contrast electron donating atom or group increase the shielding and moves the resonance towards to a lower frequency. In this study, the chemical shift obtained and calculated for the hydrogen atoms of methyl groups are quite low. It is also true from the above literature data in our present study the methyl protons at C<sub>9</sub>, C<sub>14</sub> appears as a singlet with three proton integral at 176.50, 176.51 ppm.

On the other hand the isotropic chemical shift for the carbon atoms is shown in Table 5. The relationship between

the experimental chemical shift and computed GIAO/ B3LYP/ 6-31G+(d,p) levels for 13C are shown in Fig 3.



Fig 3. Computed NMR chemical shift value of 3,5dimethylpiperidine

Table 5.Experimental and theoretical chemical shifts(13C, 1H) of 3,5- Dimethylpiperidine by

B3LYP/6-31G+ (d,p) method [8 (ppm)]									
Atom position	B3LYP								
	6-31+G(d,p)	Expt							
N1	153.765								
C2	82.907	111.02							
C3	54.917	127.15							
C4	92.800	128.48							
C5	54.9	127.15							
C6	82.9	129.31							
H7	29.7								
H8	27.1								
C9	176.50								
H10	31.6								
H11	31.0	2.39							
H12	31.4	2.39							
H13	28.5	2.39							
C14	176.51								
H15	31.6	7.72							
H16	31.4								
H17	31.0								
H18	27.1								

#### **HOMO-LUMO** Analysis

This electronic absorption correspond to the transition from the ground to the first excited state and is mainly described by one electron excitation from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) [41, 42]. The HOMO is located over nitrogen and hydrogen group and the HOMO-LUMO transition implies an electron density transfer to the methyl group from heterocyclic ring to nitrogen group. Moreover, these orbital's significantly overlap in their position for DMP is shown in Fig 4. The HOMO-LUMO energy gap of DMP was calculated at B3LYP level, which reveals that the energy gap reflects the chemical activity of molecule. The LUMO as an electron acceptor (EA) represents the ability to obtain an electron (ED) and HOMO represents ability to donate an electron (ED). The ED groups to the efficient EA groups through  $\pi$ -conjugated path. The strong charge transfer interaction through  $\pi$ -conjugated bridge results in substantial ground state Donor-Acceptor (DA) mixing and the appearance of a charge transfer band in the electron absorption spectrum. HOMO energy= -0.3273 a LUMO energy= -0.1743 a.u HOMO-LUMO energy gap = -0.1529 a.u.



Fig 4. HOMO-LUMO plot of 3,5-dimethylpiperidine

The calculated self- consistent field (SCF) energy of DMP is -327.49053656a.u. The HOMO and LUMO energy gap explains the fact that eventual charge transfer interaction is taking place within the molecule.

#### Vibrational Spectra

From the structural point of view the title compound is assumed to have Cs point group symmetry.

The 48 fundamental modes of vibrations arising for DMP are classified into 33A' and 15A" species. The A' and A" species represent the in-plane and out-of-plane vibrations, respectively. For visual comparison, the observed and calculated FTIR and FT-Raman spectra of DMP at HF and DFT/ B3LYP level using 6-31+G (d,p) basis set are shown in Figs. 5 and 6, respectively. The detailed vibrational assignment of fundamental modes of DMP along with the calculated IR and Raman frequencies and normal mode descriptions (characterize by TED) are reported in Table 6.



Wave number (cm-1)

Fig. 5. Comparison of observed and calculated IR spectra of 3,5-dimethylpiperidine(a) observed in solid phase (b) calculated with HF\6-311+G(d,p) and (c) calculated with B3LYP\6-311+G(d,p).



#### Wave number (cm-1) Fig. 6. Comparison of observed and calculated Raman spectra of 3,5-dimethylpiperidine(a) observed in solid phase (b) calculated with HF\ 6-311+G(d,p)and (c) calculated with B3LYP\6-311+G(d,p).

The vibrational analysis obtained for DMP with the unscaled HF and B3LYP/6-31+G (d,p) force field are generally somewhat greater than the experimental values due to neglect of anharmonicity in real system. These discrepancies can be corrected either by computing an harmonic corrections explicitly or by introducing a scaled field or directly scaling the calculated wave numbers with proper factor [43, 44]. A tentative assignment is often made on the basis of the unscaled frequencies by assuming the observed frequencies so that they are in the same order as the calculated ones. Then, for an easier comparison to the observed values, the calculated frequencies are scaled by the scale to less than 1, to minimize the overall deviation. A better agreement between the computed and experimental frequencies can be obtained by using different scale factors for different regions of vibrations. For that purpose, we have utilized different scaling factors for all fundamental modes to obtain the scaled frequencies of the compound. The resultant scaled frequencies are also listed in Table 6.

#### **C-H Vibrations**

The heteroaromatic structure shows the presence of C-H stretching vibration in the region 3100-3000 cm-1 which is the characteristic region for the identification of such C-H stretching vibrations [45]. These vibration are not found to be affected due to the nature and position of the substituents.

Accordingly, in the present study, the band identified at 3128, and 2953 cm-1 in FT-IR and 2953, 2927 cm-1 in FT-Raman spectrum has been designated to C-H stretching vibration and the corresponding force constant contribute 94% to the TED. The C-H in-plane-bending vibrations usually occur in the region 1390-990 cm<sup>-1</sup> and are very useful for characterization purposes. Substitution patterns on the ring can be judged from the out-of-plane bending of the ring C-H in the region 900-675 cm<sup>-1</sup> and these bands are highly informative. Therefore, the IR spectrum at 1068,1063,1057 cm<sup>-1</sup> and Raman spectrum at 1067 cm<sup>-1</sup> have been assigned to ,C-H in-plane-bending mode of DMP. The C-H out-of-plane mode for DMP is observed at 874 cm<sup>-1</sup> in IR and in Raman 790,583 cm<sup>-1</sup> respectively. The observed C-H out-of-plane bending modes

show consistent agreement with the computed B3LYP and HF results.

#### **C-C** Vibrations

The C-C heteroaromatic stretching vibrations gives rise to characteristic bands in both the observed IR and Raman spectra, covering the spectral range from 1600 to 1400 cm<sup>-1</sup> [46,47]. Therefore, the C-C stretching vibrations of the title compound are found at 1620, 1563, 1487, 1414, 1398 cm<sup>-1</sup> in FTIR and in Raman 1486, 1460, 1412, 1397 cm<sup>-1</sup> are confirmed by their TED values. Most of the ring vibrational modes are affected by the substitutions in the heteroaromatic ring of DMP. In the present study, the bands observed at 800 cm-1 in the FTIR and in Raman 845 cm-1 respectively, have been designated to ring in-plane bending modes by careful consideration of their quantitative descriptions. The ring outof-plane bending modes of DMP are also listed in Table 6. The reductions in the frequencies to these modes are due to the change in force constant and the vibrations of the functional groups present in the molecule. The theoretically computed values for C-C vibrational modes by B3LYP/6-31+G (d,p) method gives excellent agreement with experimental data. **C-N Vibrations** 

In aromatic compounds, the C-N stretching vibration usually lies in the region 1400-1200 cm<sup>-1</sup>. The identification of C-N stretching frequencies is a rather difficult task. Since the mixing of vibrations is possible in this region [46]. In this study, the bands observed at 1304, 1281 cm<sup>-1</sup> in IR and 1305, 1279 cm<sup>-1</sup> in Raman spectrum have been assigned to C-N stretching vibration of DMP is presented in Table 6. These assignments are also supported by the TED values.

#### N-H vibrations

It has been observed that the presence of N-H in various molecules may be correlated with a constant of absorption bands whose position are slightly altered from one compound to another, this is because the atomic group vibrates independently of the other groups in the molecule and has its own frequency. In all the heterocyclic compounds, the N-H stretching vibrations occur in the region 3500-3200 cm<sup>-1</sup> [46]. The position of absorption in this region depends upon the degree of hydrogen bonding, and hence upon the physical state of the sample. The spectral lines assigned to N-H stretching vibration have shifted to higher region in the present system. It clearly indicates that the stretching of N-H bond upon protonation has shifted the frequency to a higher region. Another possible cause for the stretching may be due to the occurrence of N-H and C-H hydrogen bonds in the atomic sites of the pyrimidine and aniline rings. Hence, in the presence investigation, the N-H stretching vibration have been found at 3350 cm<sup>-1</sup> in Raman, which are further supported by the TED contribution of almost 100%. The in-plane and out-ofplane bending vibration of N-H group are also supported by the literature [47].

#### CH<sub>3</sub> Group Vibrations

The title molecule DMP, under consideration possesses two CH3 groups in third and fifth position of the ring. For the assignments of CH3 group frequencies one can expected that nine fundamentals can be associated to each CH3 group, namely three stretching, three bending, two rocking modes and a single torsional mode describe the motion of methyl group. The above modes are defined in Table 6. The CH<sub>3</sub> symmetric stretching frequency is identified at 2920, 2911cm<sup>-1</sup> and CH<sub>3</sub> in-plane stretching vibrations are identified at 2871cm<sup>-1</sup> in IR 2869 cm<sup>-1</sup> in Raman spectra.

Symple C         CH         CH        CH         CH         <				HF /0-31+G(a,p)		and B3LYP/6-31		1+G(d,p) calculations						
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	Symmetry species	try Observed frequencies (cm <sup>-1</sup> )		Calc frequ	ulated iencies m <sup>-1</sup> )	s Scaling frequency (cm <sup>-1</sup> )		Force constant (mDyne/A)		IR intensity (KM/Mole)		Raman activity (A <sup>4</sup> /amu)		Assignment (% TED)
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	$\mathbf{C}_{\mathbf{s}}$			(Uns	caled)	(U	<b>n</b> )							
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		FT-IR	FT- RAMAN	HF	B3LY P	HF	B3L YP	HF	B3LYP	HF	B3LYP	HF	B3LYP	
A'         3128w         -         3136         3122         3148         3127         2340         60.999         2.2041         0.0737         317.94         131.49         vCH(9)           A'         -         2927w         3337         3195         2940         2947         71530         65521         11.009         61.015         58.874         vCH(9)           A'         -         2927w         3338         3114         2945         2945         64.323         10.004         7.5676         CHs.av(9)           A'         2911w         -         3238         3114         2945         2875         62.320         20.024         24.056         0.047         7.6678         CHs.av(9)           A'         2889m         320         306         2877         2845         6.1692         5.510         0.0423         0.3103         122.37         140.34         CHs.av(7)         CHs.av(7	A'	-	3350vw	3760	3567	3367	3351	9.4670	8.5488	35.195	55.404	342.16	196.18	vNH(99)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	A'	3128vw	-	3376	3225	3138	3127	7.3362	6.6950	2.2604	0.9737	137.94	131.49	vCH(98)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	A'	2953s	2953s	3374	3222	2964	2956	7.3095	6.6639	28.721	11.009	61.015	58.874	vCH(97)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	A'	-	2927vs	3337	3195	2940	2924	7.1530	6.5521	16.945	10.308	59.624	64.873	vCH(96)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	A'	2920vs	-	3258	3112	2935	2924	6.8730	6.2827	36.782	27.148	75.066	73.366	CH <sub>3</sub> ss(95)
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	A'	2911vs	-	3253	3114	2924	2914	6.8725	6.2820	29.024	24.405	60.947	76.678	CH <sub>3</sub> ss(94)
$\Lambda'$ $ 2843$ $2844$ $2844$ $2844$ $3176$ $3028$ $2877$ $2845$ $61668$ $50019$ $33.62$ $34.612$ $2877$ $40.847$ $CH_{10}$ pcs(7), vCH(27), vK $\Lambda'$ $1620w$ - $3175$ $3027$ $2826$ $2803$ $6.539$ $9.120$ $1.4689$ $0.239$ $28.57$ $13.92$ VCC(7), vCH(23), Rsym $\Lambda'$ $1653w$ - $1606$ $1599$ $1579$ $1686$ $3.390$ $4.339$ $9.2763$ $18.18$ vCC(6), vCH(2), Rsym $\Lambda'$ $1466w$ - $1621$ $1500$ $1479$ $1463$ $1.4231$ $14510$ $1.4851$ $1.1168$ $1.1171$ $1.526$ $1.6811$ $8.1181$ $VC(75)$ , vCH(24), VCH(2), VCH(2) $\Lambda'$ $1446w$ $1.4128$ $1.4491$ $1.4128$ $1.4491$ $1.589$ $1.3118$ $1.5417$ $1.721$ VCC(75), vCH(24) $\Lambda'$ $1378m$ $1.1209$ $14311$ $14128$ $14301$	A'	2871ms	-	3228	3079	2882	2875	6.7693	6.1503	60.042	39.103	123.75	162.04	CH <sub>3</sub> ips(93)
A'       2844s       2814 w       3176       3022       2857       2845       6.1668       5.019       33.652       48.10       284.49       375.12       CH.pops(63), vCH(27), vNR1(6)         A'       1620w       -       1722       1673       1633       1624       6.5359       9.1202       1.4689       0.2393       28.577       131.92       vCC(7), vCN(23), Raym         A'       1563w       -       1696       1599       1579       1568       5.3998       4.3339       0.2904       6.3359       0.5643       3.9502       vCC(70), vCN(23), Raym         A'       1466vs       -       1621       1504       1497       14469       1.612       1.618       1.8158       vCC(5), vCH(2), vCL(2), vCH(2)         A'       1446m       1414       1400       1.501       1.479       1.522       1.724       1.512       6.4815       2.879       vCC(7), vCH(2),	A'	-	2869m	3220	3076	2877	2867	6.7683	6.1500	0.4836	0.519	28.777	40.847	CH <sub>3</sub> ips(92)
A'         2800w         -         3175         3027         2826         2803         6.1632         5.5979         5.8955         14.597         48.574         CHLopps(70), wNH(16)           A'         1656w         -         1699         1579         1568         5.399         9.120         1.4689         0.2393         28.577         131.92         vCC(60), vCN(23), Rsymd           A'         1165w         -         1620         1599         1579         1568         5.399         4.333         0.2044         6.339         9.563         3.9502         vCC(60), vCN(23), Rsymd           A'         1446ws         1621         1500         1479         1466         2.3273         1.4237         4.256         0.0861         16.094         2.1165         hNH(53), vCC(53), vCH(4)           A'         1440m         1412w         1609         1484         1419         1.4852         1.5381         1.0171         1.9522         1.721         vCC(75), vCH(24)           A'         1398ms         13797         1.324         1.588         1.54.17         0.1588         0.0131         1.0548         0.7301         vCC(75), vCH(24)           A'         1304w         1305w         1471         1	A'	2843s	2841w	3176	3028	2857	2845	6.1668	5.6019	33.632	34.612	284.49	375.12	CH <sub>3</sub> ops(63), vCH(27), vNC (10)
A'         1620w         -         1722         1673         1633         1624         6.5399         9.1202         1.4689         0.2393         28.577         131.92         vCC(77), vCN(23), Raym           A'         1563w         -         1669         1599         1579         1568         5.3998         4.8339         0.2904         6.3599         0.5643         3.9502         vCC(60), vCR(26), Raym           A'         14487vs         1486v         1621         1500         1479         1469         1.6412         1.4214         4.6189         3.9913         2.9763         1.818         vCC(61), vCR(23), vCH(2           A'         1.444m         1414u         1480         1484         1428         1.439         1.0364         1.0161         1.0717         1.9522         1.723         CCC(75), vCH(24)           A'         1339m         1.604         1.481         1410         1.589         1.3184         1.2364         1.538         0.0181         0.4751         1.214         1.0154         0.7715         CH.jap/C3), Raym(11)           A'         1340w         1333m         1.545         1417         1355         1.345         1.633         3.0275         K.504         7.1139 <t< td=""><td>A'</td><td>2800w</td><td>-</td><td>3175</td><td>3027</td><td>2826</td><td>2803</td><td>6.1632</td><td>5.5979</td><td>58.935</td><td>53.585</td><td>14.597</td><td>48.574</td><td>CH<sub>3</sub>ops(70), vNH(16)</td></t<>	A'	2800w	-	3175	3027	2826	2803	6.1632	5.5979	58.935	53.585	14.597	48.574	CH <sub>3</sub> ops(70), vNH(16)
A'         1563w         -         1696         1599         1579         1568         5.3998         4.8339         0.2904         6.3359         0.5643         3.9502         vCC(60), vCH(26), Raym           A'         1487vs         1486w         1627         1504         1497         1448         1.4233         46.189         3.9913         9.2763         18.158         VCC (61), vCH(26), Raym           A'         1466ws         -         1618         1485         1471         1463         1.6332         1.9529         11.224         15.162         6.4815         28.798         VCC(57), CH3s(25), CH(4)           A'         144m         1412w         1619         1484         1428         1419         1.5859         1.3812         0.1041         1.0717         1.9522         17.291         VCC(57), CH424           A'         1378m         -         1549         1420         1390         1384         1.8264         1.3388         0.0181         1.0755         2.1727         CH3pb(73), Rasym(11)           A'         134ww         1343         1.421         13575         1.2264         1.3879         1.2266         0.2382         3.2612         3.2327         1.6185         1.6633	A'	1620w	-	1722	1673	1633	1624	6.5359	9.1202	1.4689	0.2393	28.577	131.92	vCC(77), vCN(23),Rsymd(10)
$\Lambda'$ 1487w         1486w         1627         1504         1497         1486         2.3213         1.4233         46.189         3.9913         9.2763         18.158         vCC (61), vCN(22), vCH ( $\Lambda'$ 1460ms         1618         1470         1469         1.632         1.4577         4.2565         0.0861         16.094         2.1165         bNH55), vCC(25), vCH ( $\Lambda'$ 1414m         1412w         1609         1484         1428         1419         1.5859         1.3312         0.1046         1.0717         1.9522         1.7291         wCC(75), wCH (24) $\Lambda'$ 1378m         -         1549         1420         1390         1384         1.8524         1.5388         1.6471         0.1385         1.318         1.0475         2.1737         5.1795         CH <sub>16</sub> pb(74),bCH(20) $\Lambda'$ 1.340w         1330b         1470         1388         1309         2.7862         2.3202         7.7139         1.0326         CN(64)         CH <sub>16</sub> pC(24)         L460(4)         L <sub>16</sub> pC(24)         L460(20)         L483         L483         1.423         1.423         L460         1.636         L <sub>16</sub> pC(3), KR(20)         L483         L460         L460	A'	1563w	-	1696	1599	1579	1568	5.3998	4.8339	0.2904	6.3359	0.5643	3.9502	vCC(60), vCH(26), Rasymd(12)
A'         1466vs         -         1621         1500         1479         1449         1.6432         1.477         4.2565         0.0861         16.094         2.1165         bNH(55), vCC(35), vCH(4)           A'         -         144m         1412w         1600         1884         1428         11585         1.3512         0.1046         1.0717         19.522         17.21         vCC(75), vCH(24)           A'         1398ms         1397w         1604         1481         1410         1400         1.585         1.351         0.1046         1.0717         19.522         1.737         CVC(75), vCH(24)           A'         1378m         -         1549         1531         1535         1.755         1.4891         2.3582         2.6126         5.6633         12.496         CH;apb(73), Raym(11)           A'         1304w         1305w         1338         1309         2.7836         2.2826         3.2027         8.674         7.7139         10.826         vCN(63), CH;apb(73), Raym(11)           A'         1280w         1261w         1393         1341         1275         1244         1284         1275         1246         135378         vCN(3), CH;apb(73), Raym(21), bC           A'	A'	1487vs	1486w	1627	1504	1497	1486	2.3273	1.4233	46.189	3.9913	9.2763	18.158	vCC (61), vCN(22), vCH (14)
A'         -         1460ms         1618         1485         1471         1463         1.632         1.9529         11.224         15.162         6.4815         28.798         VCC(57), CH3ss(25), CH(           A'         1414m         1412w         1609         1484         142         1419         1.589         1.3812         0.1044         10717         19.522         17.201         VCC(75), VCH (24)           A'         1398ms         1.549         1420         1390         1384         1.826         1.5358         0.0181         0.4755         2.1737         5.1795         CH.ipb(74),bCH(20)           A'         1304w         1330m         1545         1417         1355         1434         1.7652         1.4891         2.382         2.6126         5.6633         12.496         CH.ipb(74),bCH(20)           A'         1260w         1304         1301         1391         1292         13797         32.225         57.800         6.8031         55.375         VCN(64) CH392(20), Rsy           A'         1260w         1353         1274         1204         1897         12.266         0.7796         0.1112         10.759         9.0513         CH.sp6(7), Rtrigd(2), DC           A'	A'	1466vs	-	1621	1500	1479	1469	1.6432	1.4577	4.2565	0.0861	16.094	2.1165	bNH(55), vCC(35), v CH(10)
A'         1414m         1412w         1609         1484         1428         1419         1.5859         1.3812         0.1046         1.0717         19.522         17.291         vCC(75), vCH (24)           A'         1398ms         1397w         1604         1481         1410         1300         1588         15.417         0.1548         0.7301         vCC(75), vCH (24)           A'         1330w         1343m         1545         1417         1355         1355         0.0181         0.4755         2.1737         5.1795         CH <sub>3</sub> bp(A), CR(76), bNH(27)           A'         1340w         1343m         1545         1417         1358         1381         1309         2.7836         2.2826         3.2927         8.6574         7.119         10.826         vCN(64) CH <sub>4</sub> pc2(0), RBy           A'         1280w         12717         1294         1887         1.2266         0.7976         0.1112         10.826         vCN(64) CH <sub>3</sub> pc2(0), RSy           A'         1184m         -         1289         1182         1194         1187         1.5628         1.3135         4.8196         7.1241         2.541         7.375         1.5316         CH <sub>4</sub> pp(0), RBy gA           A'         1126m	A'	-	1460ms	1618	1485	1471	1463	1.6332	1.9529	11.224	15.162	6.4815	28.798	vCC(57), CH3ss(25), CH(18)
A'       1398ms       1397w       1604       1481       1410       1400       1.5852       1.3504       11.588       15.417       0.1548       0.7301       vCC(70, bNH(27)         A'       1378m       -       1549       1420       1390       1384       18264       1.5358       0.0181       0.4755       2.1737       5.1795       CH <sub>1</sub> ph(74),bCH(20)         A'       1340w       1335w       1470       1398       1318       1070       2.7836       2.2826       3.2027       8.6574       7.7139       10.826       vCN(64) CH <sub>1</sub> ps(20), Rsy         A'       1260w       1276       1264       1879       1286       0.7796       0.1112       10.759       9.0513       CH <sub>2</sub> shp(67), Rsymp(21), bC         A'       -       1196w       1333       1274       1204       1197       1.266       0.7796       0.1112       10.759       9.0513       CH <sub>2</sub> shp(67), Rsymp(21), bC         A'       1184m       -       1231       1161       1166       1.9522       1.8374       10.162       0.0582       3.576       1.6986       CH <sub>3</sub> sph(60), BC/2(7)         A'       1120m       1142       1058       1137       1124       1.0941       0.0582       <	A'	1414m	1412w	1609	1484	1428	1419	1.5859	1.3812	0.1046	1.0717	19.522	17.291	vCC(75), vCH (24)
A'         1378m         -         1549         1420         1390         1384         1.8264         1.5358         0.0181         0.4755         2.1737         5.1795         CH4jpb(74), JCH(20)           A'         1340w         1343         11545         1417         1335         1345         1.7652         1.4891         2.3882         2.6126         5.6633         12.496         CH4jpb(74), JCH(20)         Rsymp(17)           A'         1281w         1279w         1439         1360         1298         1289         2.8001         3.7879         32.295         57.800         6.8031         55.375         vCN(63), CH4jps(23), Rky           A'         1260w         1261v         1396         1304         1275         1264         18.879         1.2266         0.7766         0.1112         10.739         9.0513         CH4sb(67), Rsym(21), bC           A'         1184m         -         1289         1182         1194         1187         1.5628         1.3135         4.8196         7.1244         2.241         9.7258         CH3pb(67), Rsym(21), bC           A'         1120m         1142         1058         1137         1124         1.0946         0.9711         0.2008         0.0298	Α'	1398ms	1397w	1604	1481	1410	1400	1.5852	1.3504	11.588	15.417	0.1548	0.7301	vCC(76) bNH(27)
A'         1340vw         1343m         1545         1417         1355         1345         1.7652         1.4891         2.3582         2.6126         5.6633         12.496         CH:ipb(73), tRasym(11)           A'         1304w         1305w         1470         1398         1318         1309         2.7836         2.2826         3.2027         8.6574         7.7139         10.826         vCN(64), CH:ips(20), tRsym(21), tRs	A'	1378m	-	1549	1420	1390	1384	1.8264	1.5358	0.0181	0.4755	2.1737	5.1795	$CH_{3}ipb(74),bCH(20)$
A'         1304w         1305w         1470         1398         1318         1309         2.7836         2.2826         3.2027         8.6574         7.7139         10.826         vCN(64) (H_ijps(20), IRyy           A'         1281w         1279w         1439         1360         1298         12800         3.7879         52.295         57.800         6.8031         55.375         vCN(64) (H_ijps(20), IRyy           A'         1261w         1396         1304         1275         1264         18.579         12.266         0.7790         0.1112         110.759         9.0513<	Α'	1340vw	1343m	1545	1417	1355	1345	1.7652	1.4891	2.3582	2.6126	5.6633	12.496	$CH_{3}ipb(73)$ , tRasym(11)
A'       1281w       1279w       1439       1360       1298       1289       2.8001       3.7879       32.295       57.800       6.8031       55.375       vCN(63). CH;jps(23), Rtr         A'       1260w       1261 vw       1396       1304       1275       1264       1.8579       1.2266       0.7796       0.1112       10.759       9.0513       CH;sb(67), Rasym(20)         A'       1196w       1333       1274       1204       1199       3.8061       3.3230       0.8987       0.2241       17.376       15.316       CH;sb(61), Rsym(21), bC         A'       1161m       1231       1161       1176       1166       1.9522       1.8374       10.162       0.0582       3.576       16.986       CH;spb(60), bCC(27)         A'       1120w       1120m       1124       1094       0.9711       0.2008       0.0275       0.0096       Rigd(62), CH;27), DC         A'       1111w       -       1141       1056       1126       1115       1.0942       0.9646       0.3388       3.3024       0.0275       0.0096       Rigd(62), CH;jpr(21), CC         A'       1068v       1067       1082       1019       1078       1072       1.1732       3.8066 <td>A'</td> <td>1304w</td> <td>1305w</td> <td>1470</td> <td>1398</td> <td>1318</td> <td>1309</td> <td>2.7836</td> <td>2.2826</td> <td>3.2027</td> <td>8.6574</td> <td>7.7139</td> <td>10.826</td> <td><math>vCN(64) CH_3ips(20), tRsymd(14)</math></td>	A'	1304w	1305w	1470	1398	1318	1309	2.7836	2.2826	3.2027	8.6574	7.7139	10.826	$vCN(64) CH_3ips(20), tRsymd(14)$
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	A'	1281w	1279w	1439	1360	1298	1289	2.8001	3.7879	32.295	57.800	6.8031	55.375	vCN(63), CH <sub>3</sub> ips(23), tRtrigd(12)
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	A'	1260w	1261vw	1396	1304	1275	1264	1.8579	1.2266	0.7796	0.1112	10.759	9.0513	CH <sub>3</sub> sb(67), Rasym(20)
A'       1184m       -       1289       1182       1194       1187       1.5628       1.3135       4.8196       7.1244       2.241       9.7258       CH <sub>3</sub> opb(67), Rtrigd(22), bd         A'       1161m       1231       1161       1176       1166       1.9522       1.8374       10.162       0.0582       3.576       16.986       CH <sub>3</sub> opb(60), bCC(27)         A'       1131s       -       1174       1097       1154       1135       1.4233       1.2468       16.973       29.360       6.991       14.360       Rasym(61), bCH(22), DK         A'       1110w       -       1141       1056       1126       1115       1.0942       0.9646       0.8388       3.3024       0.0275       0.0096       Rtrigd(62), CH <sub>4</sub> jpr(33), bCH         A'       1068w       1067w       1082       1019       1078       1072       1.1732       3.8066       0.3718       7.0940       1.4823       2.0672       bCH(47), CH <sub>3</sub> jpr(33), bCH         A'       1063w       -       1025       966       1068       1060       1.131       0.9117       1.000       1.4337       4.777       3.022       bCH(45), CH <sub>3</sub> opb(30)         A''       981w       -       965	A'	-	1196w	1353	1274	1204	1199	3.8061	3.3230	0.8987	0.2541	17.376	15.316	CH <sub>3</sub> sb(61), Rsymd(21), bCH(11)
A'1162m1161m12311161117611661.95221.837410.1620.05823.57616.986CH <sub>3</sub> opb(60), bCC(27)A'1131s-11741097115411351.4231.246816.97329.3606.99114.360Rasym(61), bCH(22) CH <sub>3</sub> CA'1120w1120m11421058113711241.09460.97110.20080.02780.0076Rsymd(63), bCH(25), bNFA'11068vw1067w1082101511151.09420.96460.83883.30240.02750.0096Rtigd(62), CH <sub>3</sub> pr(21), CCA'1063w-10691010107310683.44081.01559.2337.38373.88712.000bCH(43), CH <sub>4</sub> pr(33), bCHA'1063w-1025966106810401.13130.911711.30014.5374.727S.0292bCH(45), CH <sub>4</sub> pp(3), bCC(23)A'1057w-102596610681.49700.5353.40320.01804.7427CH <sub>4</sub> pp(5), bCC(36)A''981w-9659279999861.75631.49700.5353.40320.01804.7427CH <sub>4</sub> pr(5), bCC(26)A''991w-7527139589440.43310.08160.37970.35704.5917CH <sub>4</sub> pp(55), bCC(30)A''-890ms-7527139589440.46460.43554.490811.1	A'	1184m	-	1289	1182	1194	1187	1.5628	1.3135	4.8196	7.1244	2.241	9.7258	CH <sub>3</sub> opb(67), Rtrigd(22), bCH(12)
A'         1131s         -         1174         1097         1154         1135         1.4233         1.2468         16.973         29.360         6.991         14.360         Rasym(61), bCH(22) CH <sub>3</sub> (           A'         1120w         1120m         1142         1058         1137         1124         1.0946         0.9711         0.2008         0.0278         0.0375         0.04057         Rsym(63), bCH(25), bNF           A'         11068w         1067w         1082         1019         1078         1072         1.1732         3.8066         0.3718         7.0940         1.4830         Rsym(d), bCH(25), bNF           A'         1063w         -         1069         1010         1073         1068         3.4408         1.0155         9.2533         7.3837         3.8387         12.000         bCH(45), CH <sub>3</sub> pr(53), bCH           A'         1057w         -         1025         966         1068         1.060         1.133         0.9117         11.300         14.537         4.7727         3.0292         bCH(45), CH <sub>3</sub> pr(53), bCC           A''         977w         -         782         734         985         980         0.4314         0.4331         0.0816         0.3797         0.5351 <th< td=""><td>A'</td><td>1162m</td><td>1161m</td><td>1231</td><td>1161</td><td>1176</td><td>1166</td><td>1.9522</td><td>1.8374</td><td>10.162</td><td>0.0582</td><td>3.576</td><td>16.986</td><td>CH<sub>3</sub>opb(60), bCC(27)</td></th<>	A'	1162m	1161m	1231	1161	1176	1166	1.9522	1.8374	10.162	0.0582	3.576	16.986	CH <sub>3</sub> opb(60), bCC(27)
A'         1120w         1121         1058         1137         1124         1.0946         0.9711         0.2008         0.0298         0.9379         0.4057         Rsymd(63), bCH(25), bNE           A'         1111w         -         1141         1056         1126         1115         1.0942         0.9646         0.8388         3.3024         0.0275         0.0096         Rtrigd(62), CH <sub>3</sub> ipr(21), CC           A'         10668vw         1067w         1082         1019         1078         1072         1.1732         3.8066         0.3718         7.0940         1.4823         20.672         bCH(47), CH <sub>3</sub> ipr(3), bCH           A'         1063w         -         1025         966         1068         1060         1.1313         0.9117         11.300         1.4537         4.7727         3.0292         bCH(45), CH <sub>3</sub> op(50)           A"         981w         -         965         927         999         986         1.7563         1.4970         0.535         3.4032         0.0180         4.7427         CH <sub>3</sub> ipr(52), bCC(36)           A"         -         950w         762         718         969         955         0.6863         1.1834         22.389         13.524         4.6271         6.644	A'	1131s	-	1174	1097	1154	1135	1.4233	1.2468	16.973	29.360	6.991	14.360	Rasym(61), bCH(22) CH <sub>3</sub> opb(11)
A'1111w-11411056112611151.09420.96460.83883.30240.02750.0096Rtrigd(62), CH_ajpr(21), CCA'1068vw1067w10821019107810721.17323.80660.37187.09401.482320.672bCH(47), CH_ajpr(3), bCHA'1063w-10691010107310683.40881.01559.25337.38373.838712.000bCH(47), CH_ajpr(3), bCHA'1057w-10259661068106061.13130.911711.30014.5374.77273.0292bCH(45), CH_opb(30)A''981w-9659279999861.75631.49700.5353.40320.01804.7427CH_ajpr(53), bCC(26)A''977w-7827349859800.48140.43310.08160.37970.35704.5917CH_ajpr(55), bCC(20)A''977w-7827139589440.64630.436544.90864.5894.32604.7547CH_apr(55), bCC(20)A''940w-7527139589440.64630.436541.90865.26011.117 $\sigma$ CH(40), CH_appt(25), bCC(22) $\omega$ Nt(1A''940w-7535308108020.93310.84933.32631.83763.02924.5256bCC(46), CH_appt(25), bCC(22) $\omega$ Nt(1)A''-845ms612604855847	A'	1120w	1120m	1142	1058	1137	1124	1.0946	0.9711	0.2008	0.0298	0.9379	0.4057	Rsymd(63), bCH(25), bNH(10)
A'       1068vw       1067w       1082       1019       1078       1072       1.1732       3.8066       0.3718       7.0940       1.4823       20.672       bCH(47), CH <sub>3</sub> ipr(33), bCH         A'       1063w       -       1069       1010       1073       1068       3.4408       1.0155       9.2533       7.3837       3.8387       12.000       bCH(47), CH <sub>3</sub> ipr(33), bCH         A'       1057w       -       1025       966       1068       1060       1.1313       0.9117       11.300       14.537       4.7727       3.0292       bCH(47), CH <sub>3</sub> ipr(52), bCC(36)         A''       981w       -       965       927       999       986       1.7663       1.4970       0.535       3.4032       0.0180       4.7427       CH <sub>3</sub> ipr(52), bCC(26)         A'''       977w       -       782       734       985       980       0.4814       0.4331       0.0816       0.3797       0.3570       4.5917       CH <sub>3</sub> ipr(53), bCC(25)         A'''       940w       -       752       713       958       944       0.6463       0.4365       44.908       64.589       4.3260       4.7547       CH <sub>3</sub> opr(55), oCC(30)         A'''       940w       -       7	A'	1111w	-	1141	1056	1126	1115	1.0942	0.9646	0.8388	3.3024	0.0275	0.0096	Rtrigd(62), CH <sub>3</sub> ipr(21), CC (12)
A'1063w-10691010107310683.44081.01559.25337.38373.838712.000bCH (32), CC(23) CH <sub>3</sub> opbA'1057w-1025966106810601.13130.911711.30014.5374.77273.0292bCH(45), CH <sub>3</sub> opb(30)A"981w-9659279999861.75631.49700.5353.40320.01804.7427CH <sub>3</sub> ipr(52), bCC(36)A"977w-7827349800.48140.43310.08160.37970.35704.5917CH <sub>3</sub> ipr(55), bCC(25)A"-950w7627189699550.68631.183422.38913.5244.62716.6440CH <sub>3</sub> opr(55), bCC(20)A"940w-7527139589440.64630.436544.90864.5894.32604.7547CH <sub>3</sub> opr(55), bCC(20)A"940w-7527139589440.64630.436544.90864.5894.32604.7547CH <sub>3</sub> opr(55), bCC(20)A"845ms6126048558470.44260.31152.19830.524011.117ocH(40), CH <sub>3</sub> opb(28)A"-845ms6126048558470.46260.31152.093215.1281.81427.6809bCC(46), CH <sub>3</sub> opb(23)A"-790m5495117997950.60090.760033.2351.55512.1501	A'	1068vw	1067w	1082	1019	1078	1072	1.1732	3.8066	0.3718	7.0940	1.4823	20.672	bCH(47), CH <sub>3</sub> ipr(33), bCH(46)
A' $1057w$ - $1025$ $966$ $1068$ $1060$ $1.1313$ $0.9117$ $11.300$ $14.537$ $4.7727$ $3.0292$ $bCH(45), CH_3opb(30)$ A" $981w$ - $965$ $927$ $999$ $986$ $1.7563$ $1.4970$ $0.535$ $3.4032$ $0.0180$ $4.7427$ $CH_{3ipr(52), bCC(36)}$ A" $977w$ - $782$ $734$ $985$ $980$ $0.4814$ $0.4331$ $0.0816$ $0.3797$ $0.3570$ $4.5917$ $CH_{3ipr(52), bCC(20)$ A" $940w$ - $752$ $713$ $958$ $944$ $0.6463$ $0.14355$ $44.908$ $64.589$ $4.3260$ $4.7547$ $CH_{3opr(55), bCC(20)$ A" $940w$ - $752$ $713$ $958$ $944$ $0.6463$ $0.4365$ $44.908$ $64.589$ $4.3260$ $4.7547$ $CH_{3opr(55), bCC(20)$ A" $874vs$ - $730$ $651$ $884$ $879$ $0.4923$ $0.5286$ $10.145$ $2.1983$ $0.5240$ $11.117$ $ocH(40), CH_{3opr(52), bCC(22)$ A"- $845ms$ $612$ $604$ $855$ $847$ $0.4626$ $0.3115$ $20.932$ $15.128$ $1.8142$ $7.6809$ $bCC(46), CH_{3opr(23)}$ A"- $790m$ $549$ $511$ $799$ $795$ $0.6009$ $0.7600$ $33.235$ $1.5951$ $2.1501$ $6.4694$ $ocH(55), bCC(22) oNH(1)$ A"- $790m$ $549$ $511$ $799$ $745$ $0.4760$ $0.4328$ $0.14$	A'	1063w	-	1069	1010	1073	1068	3.4408	1.0155	9.2533	7.3837	3.8387	12.000	bCH (32), CC(23) CH <sub>3</sub> opb(13)
A"981w-9659279999861.75631.49700.5353.40320.01804.7427CH_3ipr(52), bCC(36)A"977w-7827349859800.48140.43310.08160.37970.35704.5917CH_3ipr(52), bCC(20)A"-950w7627189699550.68631.183422.38913.5244.62716.6440CH_3opr(65), bCC(20)A"940w-7527139589440.64630.436544.90864.5894.32604.7547CH_3opr(55), wCC(30)A"947ws-7306518848790.49230.528610.1452.19830.524011.117wcH(40), CH_3opr(23)A"-845ms6126048558470.46260.311520.93215.1281.81427.6809bCC(46), CH_3opr(23)A"-790m5495117997950.60090.760033.2351.59512.15016.4694wcH(55), bCC(22) wNH(1A"-743ms742m5065067507450.47600.43280.14300.0010.11371.2638IRtrigd(44), wNH(30), wCIA"-634w4163446446390.26010.14400.055536.6600.00483.8000IRasymd(47), CH_3opr(20)A"-583s3132675955880.15990.106623	A'	1057w	-	1025	966	1068	1060	1.1313	0.9117	11.300	14.537	4.7727	3.0292	bCH(45), CH <sub>3</sub> opb(30)
A"977w-7827349859800.48140.43310.08160.37970.35704.5917 $CH_{3}pr(63), bCC(25)$ A"-950w7627189699550.68631.183422.38913.5244.62716.6440 $CH_{3}opr(65), bCC(20)$ A"940w-7527139589440.64630.436544.90864.5894.32604.7547 $CH_{3}opr(55), \omegaCC(30)$ A"874vs-7306518848790.49230.528610.1452.19830.524011.117 $\omega CH(40), CH_{3}opb(28)$ A"-845ms6126048558470.46260.311520.93215.1281.81427.6809bCC(46), $CH_{3}opt(23)$ A"-845ms6126048558470.46260.311520.93215.1281.81427.6809bCC(48), $CH_{3}opt(23)$ A"-790m5495117997950.60090.760033.2351.59512.15016.4694 $\omega CH(55), bCC(22) \omega NH(1)$ A"-743ms742m5065067507450.47600.43280.14300.0010.11371.2638tRtrigd(44), $\omega NH(30), \omega CIA"-634w4163446446390.26010.14040.052536.6960.00483.8000tRasymd(43), oCH (29)A"-583s3332675955880$	A"	981w	-	965	927	999	986	1.7563	1.4970	0.535	3.4032	0.0180	4.7427	CH <sub>3</sub> ipr(52), bCC(36)
A"-950w7627189699550.68631.183422.38913.5244.62716.6440 $CH_{3}opr(65), bCC(20)$ A"940w-7527139589440.64630.436544.90864.5894.32604.7547 $CH_{3}opr(55), \omega CC(30)$ A"874vs-7306518848790.49230.528610.1452.19830.524011.117 $\omega CH(40), CH_{3}opt(28)$ A"-845ms6126048558470.46260.311520.93215.1281.81427.6809bCC(46), CH_{3}opt(23)A"-845ms6126048558470.46260.311520.93215.1281.81427.6809bCC(46), CH_{3}opt(23)A"-790m5495117997950.60090.760033.2351.59512.15016.4694 $\omega CH(55), bCC(22) \omega NH(1)$ A"-743ms742m5065067507450.47600.43280.14300.0010.11371.2638IRtrigd(44), $\omega NH(30), \omega CIA"-634w4163446446390.26010.14040.052536.6960.00483.8000IRasymd(47), CH_3opr(20)A"-583s3332675955880.15990.106623.2621.54310.63510.9143\omega CH (57), \omega CC (32)A"-583s3332675955880.$	A"	977w	-	782	734	985	980	0.4814	0.4331	0.0816	0.3797	0.3570	4.5917	CH <sub>3</sub> ipr(63), bCC(25)
A"940w-752713958944 $0.6463$ $0.4365$ $44.908$ $64.589$ $4.3260$ $4.7547$ $CH_{3}opr(55)$ , $\omega CC(30)$ A"874vs-730651884879 $0.4923$ $0.5286$ $10.145$ $2.1983$ $0.5240$ $11.117$ $\omega CH(40)$ , $CH_{3}opb(28)$ A"-845ms612604855847 $0.4626$ $0.3115$ $20.932$ $15.128$ $1.8142$ $7.6809$ $bCC(46)$ , $CH_{3}opr(23)$ A"800ms-553530810802 $0.9331$ $0.8493$ $3.3263$ $1.8376$ $3.0292$ $4.5256$ $bCC(48)$ , $\omega CH(32)$ A"-790m549511799795 $0.6009$ $0.7600$ $33.235$ $1.5951$ $2.1501$ $6.4694$ $\omega CH(55)$ , $bCC(22)$ $\omega NH(1)$ A"743ms742m506506750745 $0.4760$ $0.4328$ $0.1430$ $0.001$ $0.1137$ $1.2638$ tRtrigd(44), $\omega NH(30)$ , $\omega CIA"-634w4163446446390.26010.14040.052536.6960.00483.8000tRasymd(47), CH3opr(20)A"-583s3332675955880.15990.106623.2621.54310.63510.9143\omega CH(57), \omega CC(32)A"-2812575635590.11940.10651.07850.07180.41312.3639\omega NH(60), \omega CH(35)$	A"	-	950w	762	718	969	955	0.6863	1.1834	22.389	13.524	4.6271	6.6440	CH <sub>3</sub> opr(65), bCC(20)
A" $874vs$ - $730$ $651$ $884$ $879$ $0.4923$ $0.5286$ $10.145$ $2.1983$ $0.5240$ $11.117$ $\omega CH(40), CH_{3}opb(28)$ A"- $845ms$ $612$ $604$ $855$ $847$ $0.4626$ $0.3115$ $20.932$ $15.128$ $1.8142$ $7.6809$ $bCC(46), CH_{3}opt(23)$ A" $800ms$ - $553$ $530$ $810$ $802$ $0.9331$ $0.8493$ $3.3263$ $1.8376$ $3.0292$ $4.5256$ $bCC(48), \omega CH(32)$ A"- $790m$ $549$ $511$ $799$ $795$ $0.6009$ $0.7600$ $33.235$ $1.5951$ $2.1501$ $6.4694$ $\omega CH(55), bCC(22) \omega NH(1)$ A"- $790m$ $549$ $511$ $799$ $795$ $0.6009$ $0.7600$ $33.235$ $1.5951$ $2.1501$ $6.4694$ $\omega CH(55), bCC(22) \omega NH(1)$ A" $743ms$ $742m$ $506$ $506$ $750$ $745$ $0.4760$ $0.4328$ $0.1430$ $0.001$ $0.1137$ $1.2638$ $tRtrigd(44), \omega NH(30), \omega CI$ A" $646m$ - $469$ $393$ $655$ $650$ $0.2288$ $0.2274$ $151.38$ $0.4065$ $4.9231$ $0.0011$ $tRsymd(47), CH_3opr(20)$ A"- $634w$ $416$ $344$ $644$ $639$ $0.2601$ $0.1404$ $0.0525$ $36.696$ $0.0048$ $3.8000$ $tRasymd(43), \omega CH (29)$ A"- $583s$ $333$ $267$ $595$ $588$ $0.1599$ $0.1066$ <th< td=""><td>A"</td><td>940w</td><td>-</td><td>752</td><td>713</td><td>958</td><td>944</td><td>0.6463</td><td>0.4365</td><td>44.908</td><td>64.589</td><td>4.3260</td><td>4.7547</td><td>CH<sub>3</sub>opr(55), ωCC(30)</td></th<>	A"	940w	-	752	713	958	944	0.6463	0.4365	44.908	64.589	4.3260	4.7547	CH <sub>3</sub> opr(55), ωCC(30)
$A''$ -845ms6126048558470.46260.311520.93215.1281.81427.6809bCC(46), CH <sub>3</sub> opr(23) $A''$ 800ms-5535308108020.93310.84933.32631.83763.02924.5256bCC(48), $\omega$ CH(32) $A''$ -790m5495117997950.60090.760033.2351.59512.15016.4694 $\omega$ CH(55), bCC(22) $\omega$ NH(1 $A''$ 743ms742m5065067507450.47600.43280.14300.0010.11371.2638tRtrigd(44), $\omega$ NH(30), $\omega$ Cl $A''$ 646m-4693936556500.22880.2274151.380.40654.92310.0011tRsymd(47), CH <sub>3</sub> opr(20) $A''$ -634w4163446446390.26010.14040.052536.6960.00483.8000tRasymd(43), $\omega$ CH (29) $A''$ -583s3332675955880.15990.106623.2621.54310.63510.9143 $\omega$ CH (57), $\omega$ CC (32) $A''$ -2812575635590.11940.10651.07850.07180.41312.3639 $\omega$ NH (60), $\omega$ CH (35) $A''$ 470w471s2582174894730.11240.04130.498172.4020.96401.2102 $\omega$ CC(72) $A''$ 431vw430w1531394434350.0397 <t< td=""><td>A"</td><td>874vs</td><td>-</td><td>730</td><td>651</td><td>884</td><td>879</td><td>0.4923</td><td>0.5286</td><td>10.145</td><td>2.1983</td><td>0.5240</td><td>11.117</td><td>ωCH(40), CH<sub>3</sub>opb(28)</td></t<>	A"	874vs	-	730	651	884	879	0.4923	0.5286	10.145	2.1983	0.5240	11.117	ωCH(40), CH <sub>3</sub> opb(28)
A"         800ms         -         553         530         810         802         0.9331         0.8493         3.3263         1.8376         3.0292         4.3256         bCC(48), wCH(32)           A"         -         790m         549         511         799         795         0.6009         0.7600         33.235         1.5951         2.1501         6.4694         wCH(55), bCC(22) wNH(1           A"         743ms         742m         506         506         750         745         0.4760         0.4328         0.1430         0.001         0.1137         1.2638         tRtrigd(44), wNH(30), wCl           A"         646m         -         469         393         655         650         0.2288         0.2274         151.38         0.4065         4.9231         0.0011         tRsymd(47), CH <sub>3</sub> opr(20)           A"         -         634w         416         344         644         639         0.2601         0.1404         0.0525         36.696         0.0048         3.8000         tRasymd(43), wCH (29)           A"         -         583s         333         267         595         588         0.1599         0.1066         23.262         1.5431         0.6351         0.9143	A"	-	845ms	612	604	855	847	0.4626	0.3115	20.932	15.128	1.8142	7.6809	bCC(46), CH <sub>3</sub> opr(23)
A"         743ms         742m         506         506         750         745         0.4760         0.4328         0.1430         0.001         0.1137         1.2638         tRtrigd(44), wNH(30), wCl           A"         646m         -         469         393         655         650         0.2288         0.2274         151.38         0.4065         4.9231         0.0011         tRsymd(47), CH <sub>3</sub> opr(20)           A"         646m         -         469         393         655         650         0.2288         0.2274         151.38         0.4065         4.9231         0.0011         tRsymd(47), CH <sub>3</sub> opr(20)           A"         -         634w         416         344         644         639         0.2601         0.1404         0.0525         36.696         0.0048         3.8000         tRasymd(43), wCH (29)           A"         -         583s         333         267         595         588         0.1599         0.1066         23.262         1.5431         0.6351         0.9143         wCH (57), wCC (32)           A"         575ms         -         281         257         563         559         0.1194         0.1065         1.0785         0.0718         0.4131         2.3639	A" A"	800ms	- 790m	553 549	530	810 799	802 795	0.9331	0.8493	3.3263	1.8376	3.0292	4.5256	$bCC(48), \omega CH(32)$
A"       745mis	Δ"	- 7/3ms	730m	506	506	750	7/5	0.0007	0.7000	0.1/130	0.001	0.1137	1 2638	(0CH(33), 0CC(22), 0NH(13))
A"         -         634w         416         344         644         639         0.2601         0.1404         0.0525         36.696         0.0048         3.8000         tRasymd(4), CH30F(20)           A"         -         634w         416         344         644         639         0.2601         0.1404         0.0525         36.696         0.0048         3.8000         tRasymd(3), wCH (29)           A"         -         583s         333         267         595         588         0.1599         0.1066         23.262         1.5431         0.6351         0.9143         wCH (57), wCC (32)           A"         557ms         -         281         257         563         559         0.1194         0.1065         1.0785         0.0718         0.4131         2.3639         wNH (60), wCH (35)           A"         470w         471s         258         217         489         473         0.1124         0.0413         0.4981         72.402         0.9640         1.2102         w CC(72)           A"         431vw         430w         153         139         443         435         0.0397         0.0189         3.6905         8.4208         1.2926         1.8011         w CC(71) <td>Δ"</td> <td>646m</td> <td>-</td> <td>469</td> <td>393</td> <td>655</td> <td>650</td> <td>0.2288</td> <td>0.4320</td> <td>151 38</td> <td>0.4065</td> <td>4 9231</td> <td>0.0011</td> <td>tRsymd(47), CH<sub>2</sub>opr(20)</td>	Δ"	646m	-	469	393	655	650	0.2288	0.4320	151 38	0.4065	4 9231	0.0011	tRsymd(47), CH <sub>2</sub> opr(20)
A"         -         583s         333         267         595         588         0.1599         0.1066         23.262         1.5431         0.6351         0.9143         ωCH (57), ωCI (29)           A"         -         583s         333         267         595         588         0.1599         0.1066         23.262         1.5431         0.6351         0.9143         ωCH (57), ωCI (29)           A"         557ms         -         281         257         563         559         0.1194         0.1065         1.0785         0.0718         0.4131         2.3639         ωNH (60), ωCH (35)           A"         470w         471s         258         217         489         473         0.1124         0.0413         0.4981         72.402         0.9640         1.2102         ω CC(72)           A"         431vw         430w         153         139         443         435         0.0397         0.0189         3.6905         8.4208         1.2926         1.8011         ω CC(71)           A"         -         210w         127         130         223         215         0.0102         0.0157         0.4268         18.219         0.0265         3.5212         tCH <sub>3</sub> (53)	A"	-	634w	416	344	644	639	0.2601	0.1404	0.0525	36.696	0.0048	3.8000	t Rasymd(43)  och (29)
A"         557ms         -         281         257         563         559         0.1194         0.1065         1.0785         0.0718         0.4131         2.3639         ωNH (60), ωCH (35)           A"         470w         471s         258         217         489         473         0.1124         0.0413         0.4981         72.402         0.9640         1.2102         ω CC(72)           A"         431vw         430w         153         139         443         435         0.0397         0.0189         3.6905         8.4208         1.2926         1.8011         ω CC(71)           A"         -         210w         127         130         223         215         0.0102         0.0157         0.4268         18.219         0.0265         3.5212         tCH <sub>3</sub> (53)	A"	-	5838	333	267	595	588	0.1599	0.1066	23.262	1.5431	0.6351	0.9143	$\omega CH (57), \omega CC (32)$
A"         470w         471s         258         217         489         473         0.1124         0.0413         0.4981         72.402         0.9640         1.2102         ω CC(72)           A"         431vw         430w         153         139         443         435         0.0397         0.0189         3.6905         8.4208         1.2926         1.8011         ω CC(71)           A"         -         210w         127         130         223         215         0.0102         0.0157         0.4268         18.219         0.0265         3.5212         tCH <sub>3</sub> (53)	A"	557ms	-	281	257	563	559	0.1194	0.1065	1.0785	0.0718	0.4131	2.3639	$\omega \text{CH}(67), \omega \text{CC}(52)$
A"         431vw         430w         153         139         443         435         0.0397         0.0189         3.6905         8.4208         1.2926         1.8011         ω CC(71)           A"         -         210w         127         130         223         215         0.0102         0.0157         0.4268         18.219         0.0265         3.5212         tCH <sub>3</sub> (53)	A"	470w	471s	258	217	489	473	0.1124	0.0413	0.4981	72.402	0.9640	1.2102	$\omega$ CC(72)
A"         -         210w         127         130         223         215         0.0102         0.0157         0.4268         18.219         0.0265         3.5212         tCH <sub>3</sub> (53)	A"	431vw	430w	153	139	443	435	0.0397	0.0189	3.6905	8.4208	1.2926	1.8011	$\omega CC(71)$
	A"	-	210w	127	130	223	215	0.0102	0.0157	0.4268	18.219	0.0265	3.5212	tCH <sub>3</sub> (53)
A"   190w   -   118   127   205   193   0.0087   0.0103   0.0105   0.0024   0.0262   0.2544   tCH <sub>3</sub> (52)	A"	190w	-	118	127	205	193	0.0087	0.0103	0.0105	0.0024	0.0262	0.2544	tCH <sub>3</sub> (52)

Table 6. The observed FT IR, FT-Raman and calculated(unscaled and scaled) frequencies(cm-1), IR intensity(km mol-1), Raman activity(A0 amu-1) and force constant(m dyne A0) and probable assignments(Characterized by TED) of 3,5-Dimethylpiperidine using HF/(6.31+C/(d n)) and R31 VP/(6.31+C/(d n)) calculations

Abbreviations: v - stretching; b - in-plane bending;  $\omega$  - out-of-plane bending; asymd - asymmetric; symd - symmetric; t - torsion; trig - trigonal; w - weak; vw-very week; vs - very strong; s - strong; ms - medium strong; ss - symmetric stretching; ass - asymmetric stretching; ips - in-plane stretching; ops - out-of-plane stretching; sb - symmetric bending; ipr - in-plane rocking; opr - out-of-plane rocking; opb - out-of-plane bending

The CH3 symmetric bending and CH<sub>3</sub> in-plane bending frequencies are attributed at 1260 cm<sup>-1</sup> and 1378, 1340 cm<sup>-1</sup>, in IR and in Raman spectrum 1261, 1196 cm<sup>-1</sup> and 1343 cm<sup>-1</sup> respectively. These assignments are supported by literature [46,47]. The in-plane rocking and out-of-plane rocking modes of CH3 group are found at 981, 977 cm<sup>-1</sup> and 940 cm<sup>-1</sup> in IR and in Raman spectrum 950 cm<sup>-1</sup> respectively. The bands obtained at 2843, 2800 cm<sup>-1</sup> and 1184,1162 cm<sup>-1</sup> in IR and 2841 and 1161 cm<sup>-1</sup> in Raman are assigned to CH<sub>3</sub> out-of-plane stretching and CH<sub>3</sub> out-of-plane bending modes, respectively. The assignment of the bands at 190 cm<sup>-1</sup> in IR and 210 cm<sup>-1</sup> in Raman are attributed to methyl twisting mode.

capacity (CV), entropy (S), internal heat (U) Gibb's free energy (G) and enthalpy change (H) for the compounds DMP were determined by B3LYP/6-311++G(d,p) method and were listed in Table 7. Fig. 7 depicts the correlation of heat capacity at constant pressure (Cp), Gibb's free energy (G), entropy (S) with temperature by B3LYP/6-311++G(d,p) method. Table 7 reveals that the entropies, heat capacities, constant pressure, internal heat Gibb's free energy and enthalpy changes are increasing with temperature ranging from 10 to 500 K due to the fact that the molecular vibrational intensities increases with temperature [48].

Table 7. Thermodynamic functions of 3,5- Dimethylpiperidine determined at different temperatures with B3LYP/6-311++C(d p) level

[							-	
Temperature	C <sub>V</sub> (J/K/mol)	CP	U	н	S	G	Q	ln(Q)
( <b>K</b> )		(J/K/mol)	(kJ/mol)	(kJ/mol)	(J/K/mol)	(kJ/mol)		
10.000	24.944	33.258	61.456	61.539	162.323	59.916	5.51448E+06	15.5228
20.000	25.102	33.416	61.706	61.872	185.397	58.165	8.82568E+07	18.2957
30.000	26.028	34.342	61.961	62.211	199.094	56.238	4.48622E+08	19.9216
40.000	27.470	35.785	62.228	62.561	209.165	54.194	1.43618E+09	21.0852
50.000	29.103	37.418	62.511	62.927	217.322	52.061	3.58697E+09	22.0005
60.000	30.948	39.262	62.811	63.310	224.303	49.852	7.67820E+09	22.7616
80.000	35.404	43.719	63.473	64.138	236.186	45.243	2.64785E+10	23.9996
90.000	37.909	46.223	63.840	64.588	241.479	42.855	4.47787E+10	24.5250
100.000	40.478	48.792	64.232	65.063	246.482	40.415	7.25225E+10	25.0071
110.000	43.035	51.349	64.649	65.564	251.253	37.926	1.13498E+11	25.4550
120.000	45.529	53.843	65.092	66.090	255.828	35.390	1.72748E+11	25.8751
130.000	47.931	56.245	65.559	66.640	260.233	32.810	2.56927E+11	26.2720
140.000	50.229	58.544	66.050	67.214	264.486	30.186	3.74735E+11	26.6494
150.000	52.424	60.739	66.564	67.811	268.601	27.521	5.37463E+11	27.0101
160.000	54.522	62.837	67.098	68.429	272.588	24.815	7.59656E+11	27.3561
170.000	56.533	64.847	67.654	69.067	276.458	22.069	1.05993E+12	27.6892
180.000	58.465	66.779	68.229	69.725	280.220	19.286	1.46195E+12	28.0107
190.000	60.327	68.641	68.823	70.403	283.881	16.465	1.99568E+12	28.3220
200.000	62.127	70.441	69.435	71.098	287.448	13.609	2.69879E+12	28.6238
210.000	63.870	72.185	70.065	71.811	290.927	10.717	3.61847E+12	28.9170
220.000	65.561	73.876	70.712	72.542	294.324	7.790	4.81356E+12	29.2024
230.000	67.203	75.517	71.376	73.289	297.644	4.830	6.35706E+12	29.4805
240.000	68.797	77.111	72.056	74.052	300.892	1.838	8.33925E+12	29.7519
250.000	70.345	78.660	72.752	74.831	304.072	1.187	1.08713E+13	30.0171
260.000	71.849	80.163	73.463	75.625	307.186	4.244	1.40897E+13	30.2764
270.000	73.307	81.622	74.189	76.434	310.239	7.331	1.81611E+13	30,5303
280,000	74 721	83.036	74 929	77 257	313 233	10 448	2 32889E+13	30 7790
290,000	76.091	84 406	75 683	78 094	316 171	13 595	2.97200E+13	31.0228
300,000	77 418	85 732	76 451	78 945	319.055	16 771	3 77535E+13	31 2621
310,000	78 701	87.015	77 231	79.809	321 887	19.976	4 77504F+13	31 4970
320,000	79 940	88 255	78.025	80.685	324.669	23 209	6.01454F+13	31 7277
320.000	81 138	89.452	78.830	81 574	327.404	26.469	7 54605E+13	31.9546
340,000	82 293	90.608	79.647	82 474	330.091	29.757	9.43204E+13	32 1777
350,000	83.408	91 722	80.476	83 386	332 734	33.071	1 17472E+14	32.1777
360,000	84 482	92 796	81 315	84 308	335 333	36.411	1.1772E+14 1 45803E+14	32.5772
370,000	85 516	93.831	82 165	85 242	337.890	39 778	1.43003E+14 1 80371E+14	32.0152
380.000	86 513	94 827	83.025	86 185	340.405	43 169	2.22429E+14	33.0356
390,000	87 472	95 786	83.895	87 138	342 881	46 586	2.22427E+14 2 73457E+14	33 2421
400.000	88 305	96 709	84 775	88 101	345 318	50.027	2.75457E+14	33.4457
410,000	89.282	97 597	85.663	89.072	347 717	53 492	4.09729E+14	33 6465
420,000	90.136	98.451	86 560	90.052	350.079	56.981	4.09729E+14	33.8445
420.000	90.958	00 272	87.466	91.041	352.405	60.493	4.07208E+14	34 0308
440.000	91.748	100.062	88 379	92.038	354 697	64 029	7 36318E+14	34 2326
440.000	02 507	100.002	80.377	03.042	356.054	67 587	7.30318E+14	34.2320
460.000	03 238	101.522	00 220	94.054	350.334	71 169	1.07/76E+15	34 6109
470.000	03 040	101.332	01 165	05.072	361 260	71.100	1.07470E+13	34.0100
480.000	04.616	102.234	02 100	95.075	363 520	78 305	1.27300E+13	34.7904
400.000	05 266	102.930	92.100	07 122	365 659	82 041	1.33409E+13	35 1607
500.000	95.200	103.300	93.037	97.132	367 757	85 709	1.00233E+13	35 3206

The regression factors (R2) of these observed relations of the thermodynamic functions vs. temperatures are all not less than 0.999. For the thermal energy, the regression coefficient (R2) is 0.987. The correlation equations for the thermodynamic parameters with temperature are given in the graphs. These equations are used to predict the value of any thermodynamic parameters for any temperature.

 $(C_p) = -09E + 04x^2 + 0.501x + 1.401$ 

(S) = 7E + 06x2 + 0.494x + 40.67(G) = 6E+06x2+0.0329x+40.58



Fig. 7. Correlation graphic of thermodynamic parameters and Temperature for entropy (S)heat capacity at constant pressure (Cp), Gibb's free energy(G) energy change of 3,5-dimethylpiperidine.

#### Conclusion

Based on the calculations ab initio HF and density functional theory with 6-31+G (d,p), levels, complete vibrational properties of DMP have been investigated by FT-IR and FT-Raman spectroscopy, respectively. Assignments of the vibrational spectra have been facilitated by DFT and HF calculations. A good correlation was found between the computed and experimental wavenumbers. The computed geometrical parameters are in good agreement with the observed X-ray diffraction data of similar compound. The calculated first hyperpolarizability is found to be 2.1749x10<sup>-</sup> <sup>30</sup>esu. Simultaneous IR and Raman activation of the benzene ring modes provide evidence for the charge transfer interaction between the donor and the acceptor groups. Therefore, the assignments made at higher level of the theory with higher basis set with only reasonable deviations from the experimental values, seems to be correct, HOMO and LUMO energy gap explains the eventual charge transfer interactions taking place within the molecule. The lone pair electrons which provide stabilization to the molecular structure enhance its bioactivity. Thermodynamic properties in the range from 10 to 500 K are obtained. This study demonstrates that scaled calculations are powerful approach for understanding the vibrational spectra of medium sized organic compounds.

#### References

[1] G.J.Richardo, B.C.Juan, R.A.Mario, M.Roldan, C.R.Peinado, Fernando, Spen,47 (1979) 168.

[2] B.R.Jerom, K.H. Spencer, Eur. Pat. Appl. Ep 277794 (1998).

[3] R.V. Perumal, M. Adiraj, P. Shanmugapandian, Indian drugs, 38 (2001) 156.

[4] C.F. Bochringer, G.M.B.H. Schochne, Brit. Pat. Appl. BP 866488 (1961).

[5] C.R. Ganellin, R.G. Spickett, J. Med. Chem, 8 (1965) 619.

[6] M. Nikolov, D. Stefanora, D. Chardanov, Acta Nerv. Super, 16 (1974) 264.

[7] B. Kathleen, C. Jean-Peirre, H. Andre, Eur. Pat. Appl. Ep 169139 (1986).

[8] R.E. Hagenbach, H. Gysin, Experientia, 8 (1952) 184.

[9] B. Heana, V. Dobre, I. Niculesucu-Duvaz, J. Prakt. Chem, 327 (1985) 667.

[10] I.G. Mobio, A.T. Soldatenkov, V.O. Fedrov, E.A. Ageev, N.D. Sergeeva, S. Lin, E.E. Stashenko, N.S. Prostakov, E.I. Andreeva, Khim. Farm. Zh, 23 (1989) 421.

[11] M.T. Gulluoglu, Y. Erdogdu and S. Yurdakul, J. Mol. Struct. 834 (2007) 540.

[12] Y. Erdogdu and M.T. Glluoglu, Spectrochim. Acta A 74 (2009) 162.

[13] Yu.A. Pentin and O.S. Anisimova, Opt. Spectros, 26 (1968) 35.

[14] T. Hirokawa, T. Kimura, K. Ohno, H. Murata, Spectrochim. Acta A 36 (1980) 329.

[15]G. Marcotrigiano, L. Meanbue, G.C.Pellacani, J. Mol. Struct. 30 (1976) 85.

[16] Y. Okishi, Y. Imai, K. Aida, J. Inorg. Nucl. Chem 13 (1973) 101.

[17] T.V. Titova, O.S. Anisimova, Opt, Spectros. 23 (1967) 495.

[18] D. Vedal, O. Ellestad, P. Klaboe, G. Hagen, Spectrochim Acta A 32 (1976) 877.

[19] E. Vayner, D.W. Ball, J. Mol. Struct. (THEOCHEM). 496 (2000) 175.

[20] S.Sebastain, N.Sundaraganesan, Spectrochim. Acta A 75 (2010) 941.

[21] Gaussian 09 Program, Gaussian Inc., Wallingford CT., 2009.

[22] A.D.Becke, J.Chem. Phys. 98(1993)5648-5652.

[23] C.Lee, W.Yang, R.G.Parr. Phys. Rev. B37 (1988) 785-789.

[24] P.Pulay, G. Fogarasi, G.Pongor, J.E.Boggs, A.Vargha, J. Am. chem. soc,105 (1983) 7037-047.

[25] G. Fogarasi, P.Pulay,in: J.R.Durig(Ed.) Vibrational Spectra and Structure, Vol.14, Elsevier, Amsterdam, 1985, P. 125, Chapter 3.

[26] T.Sundius, vib, spectrosc.29 (2002)89-95.

[27] MOLVIB (V.7.0):Calculation of Harmonic Force Fields and Vibrational Modes of Molecules, QCPE Program No. 807(2002).

[28] R.Ramachandran, P.Parthiban, M,Rani, S.Kabilan, Yeon Tae Jeong.Acta Crystallographica section E66 (2010) o2284.[29] P.L. Polavarapu, J. Phys. Chem. 94 (1990) 8106-8112.

[30] J.Karpagam, N.Sundaraganesan, S.Sebastain,
 S.Manoharan, M.Kurt, J. Raman Spectrosc, 41(2010)53-62.

[31] D.A.Kleinman, Phys. Rev.126(1962)1977-1979.

[32] M. Szafran, A. Komasa, E.B. Adamska, J. Mol. Struct. (THEOCHEM) 827 (2007) 101.

[33] C. James, A.A.Raj, R. Reghunathan, I. H.Joe, V.S. Jayakumar, J. Raman, Spectrosc. 37 (2006) 381.

[34] L.Jun-na, C.Zhi-rang, Y.Shen-fang, J. Zhejiang, Univ. Sci. 6B (2005) 584.

[35] A. Krushelnitsky, D. Faizullin, D. Reichert, Biopolymers 73(1), 2004, 1-15.

[36] B. Osmialowski, E. Kolehmainen, R. Gawinencki, Magn. Reson. Chem 39, 2001, 334 340.

[37] R. Marek, J. Brus, J. Tousk, L. Kovacs, D. Hockova, Magn. Reson. Chem.40, 2002, 353-360.

[38] Z. Meng. W.R. Carper, J. Mol. Struct. Theochem. 588 (2002) 45-53.

[39] H.O. Kalinowski, S. Berger, S. Brawn.Cabon-13 NMR spectroscopy, John wiley and sons, Chichester 1988.

[40] K. Pihlajer, E. Kleinpeter (Eds,), Cabon-13 Chemical shifts in structure and spectrochemical analysis, VCH publishers, Deerfield Beach. 1994.

[41] E. Kavitha, N. Sundarabganesan, S. Sebastian Ind. J. Pure Appl. Phys. 48 (2010) 20- 30.

[42] Onkar Prasad, Leena Sinha, Naveen Kumar, J. At. Mol. Sci. 1 (2010) 201-214.

[43] V.Krishnakumar, Gabor Keresztury, S. Tom Sundius, Seshadri, Spectrochim Acta 68 A (2007) 845-850.

[44] Kuppusamy Sambathkumar Spectrochim. Acta A 147 (2015) 51-66.

[45] M. Arivazhagan, K. Sambathkumar & S. Jeyavijayan, Ind. J. Pure Appl. Phys 48 (2010) 716.

[46] K.Sambathkumar, S.Jeyavijayan, M.Arivazhagan Spectrochim Acta A 147 (2015)51-66..

[47] G.Socrates, Infrared and Raman Characteristic Group Frequencies-Tables and Charts, Third ed., Wiley, Chichester, 2001.

[48] D.Cecily Mary Glory, R.Madivanane and K.Sambathkumar Elixir Comp. Chem. 89 (2015) 36730-36741.