

FT-IR, FT-Raman And UV Spectra and Ab-Initio HF and DFT Vibrational Study of 1-Propyl 4-Piperidone

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Abstract

The Fourier transform infrared spectra (FT-IR) and Fourier transform Raman spectra (FT Raman) of The 1-Propyl 4-Piperidone have been recorded in the regions 4000-400, 4000-100 cm^{-1} . The ultraviolet spectra (UV) spectra of the title molecule in the region 800-200 cm^{-1} . Utilizing the observed FT-IR and FT Raman spectra data, a complete vibrational assignments and analysis of the fundamental mode of the compound have been carried out. The optimum molecular geometry, vibrational frequencies, Infrared and Raman intensities have been calculated by Hartree-Fock (HF) with 6-311 ++G(d,p) basis set and Density functional theory (DFT) method at B3LYP level with 6-311++G(d,p) levels. The difference between the observed and scaled wave number values of most of the fundamental is very small. A detailed interpretation of the frequencies calculated at DFT levels matches well with the experimental values. Mulliken's net charges have also been calculated. Molecular frontier orbitals and thermodynamic properties have been performed by Hartree-Fock (HF) and Density functional theoretical (DFT) method

Keywords: 1-Propyl 4-Piperidone, , FTIR, FT Raman, UV, HF,DFT, HOMO-LUMO

INTRODUCTION

1-Propyl 4-Piperidone is a clear liquid in yellow colour which boiling point at 56⁰ C of 1 mm Hg pressure, has a specific gravity/density of 0.936. The molecular formula is C₈H₁₅NO. Piperidone (also known as piperidinone or azinanone) is a saturated heterocyclic organic compound containing one nitrogen atom, and a carbonyl group in the ring. 4-Piperidone is used as an intermediate in the manufacture of chemicals and pharmaceutical drugs [1].

EXPERIMENTAL

High grade sample of 1-Propyl 4-Piperidone was purchased from Avira chemicals and was used without further purification. The FTIR spectrum of the molecule was recorded using Burker IFS 66V spectrophotometer in the region 4000- 400 cm^{-1} and UV absorption spectrum using Jasco V-670 spectrometer in the region 800-200 cm^{-1} . The FT Raman spectrum of the molecule was taken from IIT using Burker RFS27 recorded in the region 4000-100 cm^{-1} . The assignments were analogue with earlier assignments reported in the literature.

COMPUTATIONAL DETAIL

The entire calculations in the present work were carried at Hartree-Fock (HF) and DFT/B3LYP levels using Gaussian 09W package [2] program with the 6-311++G(d,p) basis set function utilizing gradient geometry optimization. The vibrational modes assigned using Gauss-view molecular visualization program package [2-4] for motions observed against fundamental frequencies. B3LYP represents Becke's the parameter hybrid functional method Becke with Lee-Yang-Parr's functional relation (LYP) [5-7]. Gauss view 5.0 program, a graphical interface was used to study the vibrational assignments, and other thermodynamic properties of the molecule.

RESULTS AND DISCUSSION

MOLECULAR GEOMETRY

The molecule has 25 atoms with 3N degrees of freedom corresponding to the Cartesian coordinates of each atom in the molecule. In a non linear molecule, 3 of these degrees belong to the rotational, 3 of these degrees belong to translational motions and remaining (3N-6) corresponds to its vibrational motions. The optimized geometry of the molecule is shown in Figure 4.1 and the experimental and calculated spectra are given in Figure 4.2.

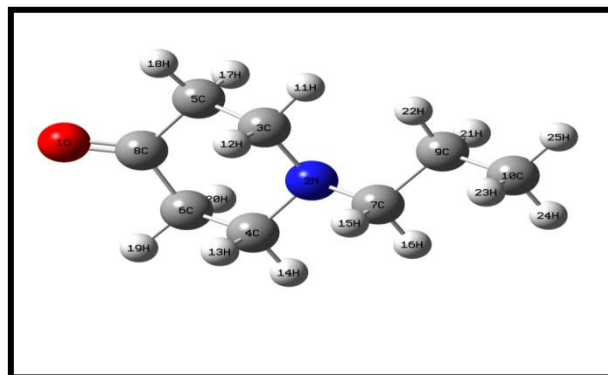


Figure 4.1 Optimized geometry of 1-Propyl 4-Piperidone

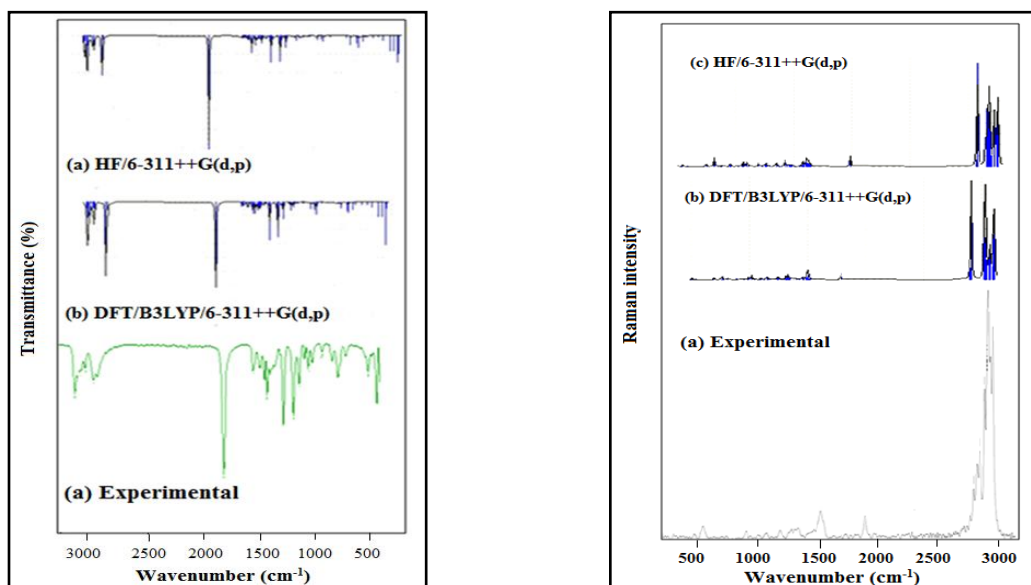


Figure 4.2 Comparison of experimental and calculated FTIR and FTRaman spectra

It has been observed that C-C bond length is 1.5037 \AA and C-H bond length is 1.0853 \AA as shown in Table 4.1. The bond length of $C_4 - C_6$ (1.52 \AA) is slightly $\sim 0.02 \text{ \AA}$ greater than $C_6 - C_8$ (1.50 \AA) due to the delocalization of electron. Due to the π bond character of the bond angle between $C_5 - C_8 - C_6$ and $C_7 - C_9 - C_{10}$ is 115.94 and 111.35 respectively. The presence of hyperconjugative interaction is arised due to bond angle of $O_1 - C_8 - C_5$ (121.89) and $N_2 - C_3 - C_5$ (111.38). On account of Oxygen and Nitrogen group present in the compound the sharing of electron between neighboring atoms occurs easily which result in increased C-C bond length.

Table 4.1 Optimized geometrical parameters bond length (\AA) and bond angle ($^\circ$) of 1-Propyl 4-Piperidone

Optimized parameters	Method/basis sets		Experimental
	HF/ 6-311++G(d,p)	DFT/B3LYP/ 6-311++G(d,p)	
Bond length			
R (3,11)	1.0812	1.0921	1.0921
R (3,12)	1.097	1.0982	1.0982
R (4,6)	1.5301	1.5256	1.5256
R (4,13)	1.0969	1.0984	1.0984
R (4,14)	1.0834	1.0969	1.0969
R (5,8)	1.5117	1.5099	1.5099
R (5,17)	1.088	1.0958	1.0958
R(5,18)	1.0831	1.0952	1.0952
R (6,8)	1.5118	1.5098	1.5098
Bond Angle			
A (3,2,4)	110.609	110.5389	110.5389
A (3,2,7)	112.9648	110.3085	110.3085
A (4,2,7)	111.9417	110.3091	110.3091
A (2,3,5)	111.3075	111.3867	111.3866
A (1,8,6)	122.8866	121.8903	121.8903

A (5,8,6)	114.2081	115.9425	115.9424
A (7,9,10)	111.9271	111.3522	111.3522

VIBRATIONAL ASSIGNMENT

The molecule has 25 atoms with $3N$ degrees of freedom corresponding to the Cartesian coordinates of each atom in the molecule. In a non linear molecule, 3 of these degrees belong to the rotational, 3 of these degrees belong to translational motions and remaining $(3N-6)$ corresponds to its vibrational motions[39]. Therefore the net number of modes of vibrations is 69. The detailed vibrational analysis of fundamental modes using HF/6-311++G(d,p) and DFT/B3LYP/6-311++G(d,p) with FT-IR and FT-Raman experimental frequencies of title molecule were presented in Table 4.2.

C=O (Carbonyl) Vibrations

The C=O stretching vibration is expected in the region $1850-1600\text{ cm}^{-1}$ [8]. In the present study, it had been observed at 1703 cm^{-1} in DFT/B3LYP level. A strong band is observed at 1714 cm^{-1} in FTIR and at 1717 cm^{-1} in FT Raman were observed representing the presence of C=O in the molecule. The out of plane bending modes of C=O bonds are observed at 507 cm^{-1} in FT-IR and 489 cm^{-1} in Raman; 487 cm^{-1} in B3LYP/6-311++G(d,p) and 500 cm^{-1} in HF/6-311++G(d,p).

CH₃ Vibrations

The CH₃ stretching vibrations is expected in the region $2845\pm 45\text{ cm}^{-1}$ and $2955\pm 20\text{ cm}^{-1}$ in which all the three C-H extend and contract in phase [9]. The CH₃ stretching vibration found in Raman spectrum intense bands at 2940 and 2874 cm^{-1} which also found in FT-IR at 2930 and 2873 cm^{-1} . The B3LYP/6-311+G(d,p) gives the frequencies values for CH₃ stretching at 2948 and 2882 cm^{-1} and the HF/6-311+G(d,p) method gives at 2935 and 2869 cm^{-1} .

The experimental frequencies of methyl out of plane bending are observed in FT-IR at 1470 , 1469 , 1132 cm^{-1} and also observed at 1480 , 1458 , 1120 cm^{-1} in FT-Raman. The B3LYP/6-311++G(d,p) and HF/6-311++G(d,p) calculations gives the CH₃ out of plane bending frequencies at 1440 , 1434 , 1432 , 1427 , 1083 and 719 cm^{-1} and 1484 , 1481 , 1471 , 1469 , 1126 and 731 cm^{-1} respectively.

CH₂ - Vibrations

The CH₂ asymmetric stretching vibration generally observed in the region $3000-2900\text{ cm}^{-1}$, while the CH₂ symmetric stretch will appear between 2900 and 2800 cm^{-1} [10]. In the present study, very strong intense band appear in the FT-Raman for CH₂ asymmetric stretching at 3198 ,

2966 and 2910 cm^{-1} and weak intense in FT-IR at 2960 and 2950 cm^{-1} . The calculated bands observed at 2960, 2959, 2950, 2927 and 2918 cm^{-1} in B3LYP/6-311++G(d,p) and 2960, 2955, 2954, 2929 and 2910 cm^{-1} in HF/6-311++G(d,p).

The CH_2 symmetric stretching vibration in FT-Raman appears at 2885 and 2874 cm^{-1} and weak intense in FT-IR at 2890, 2873 cm^{-1} . The calculated bands observed at 2889, 2887, 2884 and 2882 cm^{-1} in B3LYP/ 6-311++G(d,p) and 2890, 2886, 2884 and 2869 cm^{-1} in HF/6-311++G(d,p) method. The deformation vibrations of $-\text{CH}_2-$ group (scissoring, wagging, twisting and rocking) contribute to several normal modes in the low frequency region. Since the bending modes involving hydrogen atom attached to the central carbon falls into the 1485–645 cm^{-1} range.

C – C Vibrations

The C-C stretching frequencies are generally predicted in the region 650-1650 cm^{-1} [11]. The bands occurring at 1008 and 1009 cm^{-1} in FT-IR and FT-Raman spectra have been assigned to C-C-C out plane bending vibrations. The frequencies 994 cm^{-1} and 1012 cm^{-1} are assigned to C-C-C out of plane bending in B3LYP/6-311+G(d,p) and HF/6-311+G(d,p) respectively.

C – N Vibrations

The C-N stretching wave number is rather a difficult task since there are problems in identifying these wave numbers from other vibration. The C-N stretching absorption in the region 1200-1400 cm^{-1} [12]. The C-N stretching vibration at 1250 cm^{-1} (FTIR); 1240 cm^{-1} (FT-Raman). The theoretical observations in B3LYP/6-311++G(d,p) at 1211 cm^{-1} and HF/6-311++G(d,p) at 1251 cm^{-1} .

C-H vibrations

In the present study, C-H stretching vibrations occurs at 2950 and 2804 cm^{-1} in FTIR and 2940, 2910, 2807, 2772 and 2735 cm^{-1} in FT-Raman. The theoretical observations in B3LYP/6-311++G(d,p) at 2950, 2948, 2929, 2918, 2901, 2771, 2759 and 2757 cm^{-1} and HF/6-311++G(d,p) at 2954, 2935, 2929, 2910, 2901, 2797, 2785 and 2783 cm^{-1} respectively which is in good agreement with the literature value 2850-3000 cm^{-1} . The C-H in plane and out of plane bending occurs at 1300-1000 and 1000-750 cm^{-1} [13] respectively.

Table 4.2
 Vibrational assignments of 1-Propyl 4-Piperidone

S. No	Observed fundamentals		Calculated frequencies						Vibrational Assignments
			HF/6-311++G(d,p)			DFT/B3LYP/6-311++G(d,p)			
	FTIR	Raman	Scaled	IR intensity	Raman Intensity	Scaled	IR intensity	Raman Intensity	
1	2960	3198	2960	1.481	0.118	2960	0.379	0.168	$\nu_{as}(\text{CH}_2)$, $\nu_{as}(\text{CH}_2)$
2		2966	2955	2.501	0.188	2959	2.965	0.247	$\nu_{as}(\text{CH}_2)$, $\nu_{as}(\text{CH}_2)$
3	2950		2954	2.506	0.183	2950	1.727	0.257	$\nu_{as}(\text{CH}_2)$, $\nu_{as}(\text{CH}_2)$, $\nu(\text{CH})$
4	2930	2940	2935	3.321	0.259	2948	2.369	0.213	$\nu(\text{CH}_3)$, $\nu(\text{CH})$
5			2929	1.596	0.082	2942	1.348	0.120	$\nu_{as}(\text{CH}_2)$, $\nu_{as}(\text{CH}_2)$, $\nu(\text{CH})$, $\nu(\text{CH})$
6			2929	0.057	0.106	2927	0.038	0.038	$\nu(\text{CH})$, $\nu(\text{CH})$, $\nu_{as}(\text{CH}_2)$
7		2910	2910	0.729	0.394	2918	0.984	0.308	$\nu_{as}(\text{CH}_2)$, $\nu_{as}(\text{CH}_2)$, $\nu(\text{CH})$, $\nu(\text{CH})$
8			2901	1.359	3.526	2901	1.220	4.384	$\nu(\text{CH})$, $\nu(\text{CH})$, $\nu(\text{CH})$
9	2890	2885	2890	1.285	1.197	2889	1.393	1.427	$\nu_s(\text{CH}_2)$, $\nu_s(\text{CH}_2)$, $\nu_s(\text{CH}_2)$
10			2886	3.696	0.446	2887	3.729	1.179	$\nu_s(\text{CH}_2)$, $\nu_s(\text{CH}_2)$, $\nu_s(\text{CH}_2)$
11			2884	8.566	1.548	2884	6.052	2.367	$\nu_s(\text{CH}_2)$, $\nu_s(\text{CH}_2)$
12	2873	2874	2869	5.704	1.874	2882	4.623	2.668	$\nu(\text{CH}_3)$, $\nu_s(\text{CH}_2)$
13	2804	2807	2797	7.900	2.417	2771	3.888	2.760	$\nu(\text{CH})$, $\nu(\text{CH})$, $\nu(\text{CH})$
14		2772	2785	2.500	0.723	2759	1.259	1.106	$\nu(\text{CH})$, $\nu(\text{CH})$, $\nu(\text{CH})$
15		2735	2783	2.061	3.938	2757	1.356	3.465	$\nu(\text{CH})$, $\nu(\text{CH})$
16	1714	1717	1805	1.352	0.164	1703	1.714	0.114	$\nu(\text{C}=\text{O})$
17			1497	7.930	12.35	1449	12.17	10.24	$\xi(\text{CH}_2)$, $\xi(\text{CH}_2)$, $\xi(\text{CH}_2)$, $\xi(\text{CH}_2)$, $\xi(\text{CH}_2)$
18			1484	4.666	0.855	1440	7.448	0.300	$\gamma(\text{CH}_3)$, $\xi(\text{CH}_2)$, $\xi(\text{CH}_2)$, $\xi(\text{CH}_2)$, $\xi(\text{CH}_2)$
19	1470	1480	1481	6.138	2.725	1434	7.220	2.541	$\gamma(\text{CH}_3)$, $\xi(\text{CH}_2)$, $\xi(\text{CH}_2)$, $\xi(\text{CH}_2)$, $\xi(\text{CH}_2)$
20			1471	1.790	2.597	1432	1.888	0.825	$\gamma(\text{CH}_3)$
21	1469	1458	1469	0.429	3.315	1427	1.223	3.067	$\gamma(\text{CH}_3)$, $\xi(\text{CH}_2)$, $\xi(\text{CH}_2)$,

									$\xi(\text{CH}_2)$
22			1464	1.459	1.024	1420	1.554	0.891	$\gamma(\text{CH}_3)$, $\xi(\text{CH}_2)$, $\xi(\text{CH}_2)$, $\xi(\text{CH}_2)$
23			1446	1.468	1.013	1396	1.520	0.385	$\xi(\text{CH}_2)$, $\xi(\text{CH}_2)$
24			1437	3.909	6.817	1386	7.167	4.582	$\xi(\text{CH}_2)$, $\xi(\text{CH}_2)$
25			1427	8.396	10.61	1366	11.07	11.07	$\omega(\text{CH}_2)$, $\omega(\text{CH}_2)$,
26			1409	3.064	2.167	1348	1.822	2.271	$\beta(\text{CH}_3)$, $\omega(\text{CH}_2)$
27	1390	1400	1397	10.53	3.108	1342	23.13	2.961	$\omega(\text{CH}_2)$,
28			1373	22.32	4.014	1317	7.207	2.449	$\omega(\text{CH}_2)$,
29	1350	1360	1353	2.570	2.397	1295	2.953	0.972	$\tau(\text{CH}_2)$, $\omega(\text{CH}_2)$
30			1343	14.93	3.991	1282	15.56	6.007	$\tau(\text{CH}_2)$, $\omega(\text{CH}_2)$, $\omega(\text{CH}_2)$, $\gamma(\text{CH}_3)$
31	1330	1321	1329	49.52	8.146	1271	13.95	5.225	$\tau(\text{CH}_2)$, $\tau(\text{CH}_2)$, $\beta(\text{CH})$
32			1318	1.975	1.930	1267	2.564	2.573	$\tau(\text{CH}_2)$, $\omega(\text{CH}_2)$, $\omega(\text{CH}_2)$, $\omega(\text{CH}_2)$, $\omega(\text{CH}_2)$
33			1300	7.866	4.880	1254	58.80	3.565	$\tau(\text{CH}_2)$, $\tau(\text{CH}_2)$, $\omega(\text{CH}_2)$
34			1274	55.47	3.247	1233	5.392	6.193	$\tau(\text{CH}_2)$, $\tau(\text{CH}_2)$, $\tau(\text{CH}_2)$, $\gamma(\text{CH}_3)$
35	1250	1240	1251	1.609	0.361	1211	1.308	0.459	$\tau(\text{CH}_2)$, $\tau(\text{CH}_2)$, $\gamma(\text{CH})$, $\gamma(\text{CH})$, $\nu(\text{CN})$
36			1229	7.270	1.291	1189	6.803	0.941	$\tau(\text{CH}_2)$, $\tau(\text{CH}_2)$, $\gamma(\text{CH})$, $\gamma(\text{CH})$, $\gamma(\text{CH})$
37	1215	1211	1226	1.859	12.69	1181	4.688	7.469	$\gamma(\text{CH}_3)$, Deformation bending
40	1132		1140	4.514	1.964	1098	7.966	2.176	Deformation bending

ν -stretching, ν_s -symmetric stretching, ν_{as} -asymmetric stretching, β -in plane bending, γ -out of plane bending, ξ -scissoring, ρ -rocking, ω -wagging and τ -twisting.

THERMODYNAMIC PROPERTIES

The thermodynamic parameters for the title molecule heat capacity, entropy, rotational constants, dipole moments, SCF energy, Vibrational and vibrational zero point energies of the compound have also been computed at HF/6-311++G(d,p) and DFT/B3LYP/6-311++G(d,p) basis set and are presented in Table 5. From the table, it is clear that a minimum energy is observed for DFT method. These data provides useful information for further study when used as a reactant. These standard thermodynamic functions can be used as reference thermodynamic values to calculate charges of entropies (ΔS_T) and changes of enthalpies (ΔH_T) of the reaction.

The dipole moment and its principal inertial axes are strongly depending upon the conformation of the molecule.

Table 5
Thermodynamic Parameter of 1-Propyl 4-Piperidone

Parameters	HF / 6-311++G(d,p)	DFT/B3LYP/ 6-311++G(d,p)
SCF energy (a.u.)	-441.09953	-443.97531
Total energy (thermal) E_{total} (Kcal mol ⁻¹)	155.949	146.6
Vibrational energy, E_{vib} (Kcal mol ⁻¹)	154.172	144.822
Zero point vibrational energy (Kcal mol ⁻¹)	626233.0	585541.2
Specific heat capacity, C_v (cal mol ⁻¹ K ⁻¹)	36.588	39.46
Entropy, S (cal mol ⁻¹ K ⁻¹)	99.07	101.67
Rotational constant (GHz) X	3.8117200	3.7727919
Y	0.6134175	0.6060523
Z	0.5553882	0.5483702
Dipole moment μ (Debye) μ_x	-3.6426	3.4959
μ_y	0.4198	0.3995
μ_z	-0.2888	0.3619
Total	3.6781	3.5372

CONCLUSION

In the present study, attempts have been made to study the vibrational investigations of 1-Propyl 4-Piperidone by using HF and DFT methods. The FTIR and FTRAMAN spectrum of the sample was analyzed. The observed and calculated frequencies are found to be in good agreement. The optimized geometries, harmonic frequencies were determined and analysed both at HF and DFT/B3LYP levels of theories using 6-311++G(d,p) basis sets. The theoretical results have been compared with experimental vibrations and values obtained from DFT/B3LYP/6-311++G(d,p) level is in good agreement with the experimental values. HOMO-LUMO analyses and thermodynamical parameters such as the zero point vibrational energy, entropy, heat capacity rotational

constants have been computed out. Mullikan Atomic Charges have been calculated and properly tabulated and it is graphically represented.

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