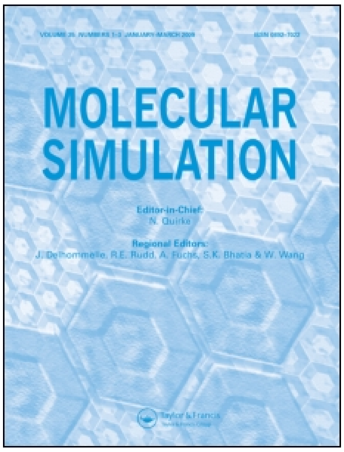

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Molecular structure, vibrational spectra and HOMO, LUMO analysis of 4-piperidone by density functional theory and *ab initio* Hartree-Fock calculations

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Molecular structure, vibrational spectra and HOMO, LUMO analysis of 4-piperidone by density functional theory and *ab initio* Hartree–Fock calculations

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Vibrational frequencies and geometrical parameters of 4-piperidone (4-PID) in the ground state have been calculated by using the Hartree–Fock (HF) and density functional methods (B3LYP) with 6-311++G(d,p) and 6-311+G(3df,2p) basis sets. These methods are proposed as a tool to be applied in the structural characterisation of 4-PID (C_5H_9NO). The title molecule has C_s point group symmetry, thus providing useful support in the interpretation of experimental IR and Raman data. The DFT-B3LYP/6-311+G(3df,2p) calculations have been found more reliable than the *ab initio* HF/6-311++G(d,p) calculations for the vibrational study of 4-PID. The calculated highest occupied molecular orbital and lowest unoccupied molecular orbital energies show that charge transfer occurs within the molecule. The theoretical spectrograms for FT-IR and FT-Raman spectra of the title molecule have been constructed.

Keywords: 4-piperidone; HF; DFT; FTIR; FT-Raman; vibrational assignments; HOMO; LUMO

1. Introduction

4-piperidone (4-PID) is an organic compound with the molecular formula C_5H_9NO. It is a heterocyclic amine with a six-membered ring containing five carbon atoms, one nitrogen atom and one oxygen atom. In recent years, there has been a growing interest pertaining to the synthesis of bioactive compounds in the field of organic chemistry. Among the family of heterocyclic compounds, nitrogen containing heterocyclic compounds especially, piperidin-4-ones presumably are gaining considerable importance owing to their varied biological properties such as antiviral, antitumour [1], analgesic [2], local anaesthetic [3,4], antimicrobial, bactericidal, fungicidal, herbicidal, insecticidal, antihistaminic, anti-inflammatory, anticancer, CNS stimulant and depressant activities [5–7].

Chiral polysubstituted piperidines represent one of the most common building blocks in natural products with biological activity [8–12] and have been identified as important therapeutic agents for the treatment of a range of diseases [1–8]. In recent years, thousands of piperidine compounds have been mentioned in clinical and pre-clinical studies directed towards the development of new drugs. As a consequence, the development of new and efficient stereo selective synthesis of not only the active compounds but also of chemically modified analogues is of major interest within medicinal chemistry.

Lijinsky and Taylor [13] reported that blocking of a-positions to that of nitrogen in 4-PID by the alkyl group had good advantages over unblocked one in improving the biological activity. Furthermore, significance of piperidin-4-ones as intermediates in the synthesis of a variety of physiologically active compounds has been reviewed by Prostakov and Gaivoronskaya [14]. The skeletal ring of piperidine nucleus can also be often found in the molecular framework of many synthetic and natural medicaments [15]. Similarly, amides are well known for their therapeutic values [16]. The chemistry of amides having a chloro-acetyl group is also very fascinating and has received significant attention through the years resulting in substantial advances. Recently FT-IR and FT-Raman spectra of 1-methyl-4-PID has been recorded and the observed bands were interpreted with the aid of normal coordinate analysis following a full structure optimisation and force field calculation based on the density functional theory (DFT) using the 6-311G(d,p) basis set [17].

To gain a better understanding of the performance and limits of HF and DFT methods as a general approach to the vibrational problems of organic molecules, we calculated harmonic frequencies of 4-PID by HF and DFT methods and compared these results with observed fundamental vibrational frequencies. In the present study, we report our results on vibrational analysis of 4-PID using the SQM force field method based on HF and DFT calculation. The aim of the present work is to check the performance of HF and B3LYP density functional force field for simulation of IR spectra of the title molecule with the use of standard

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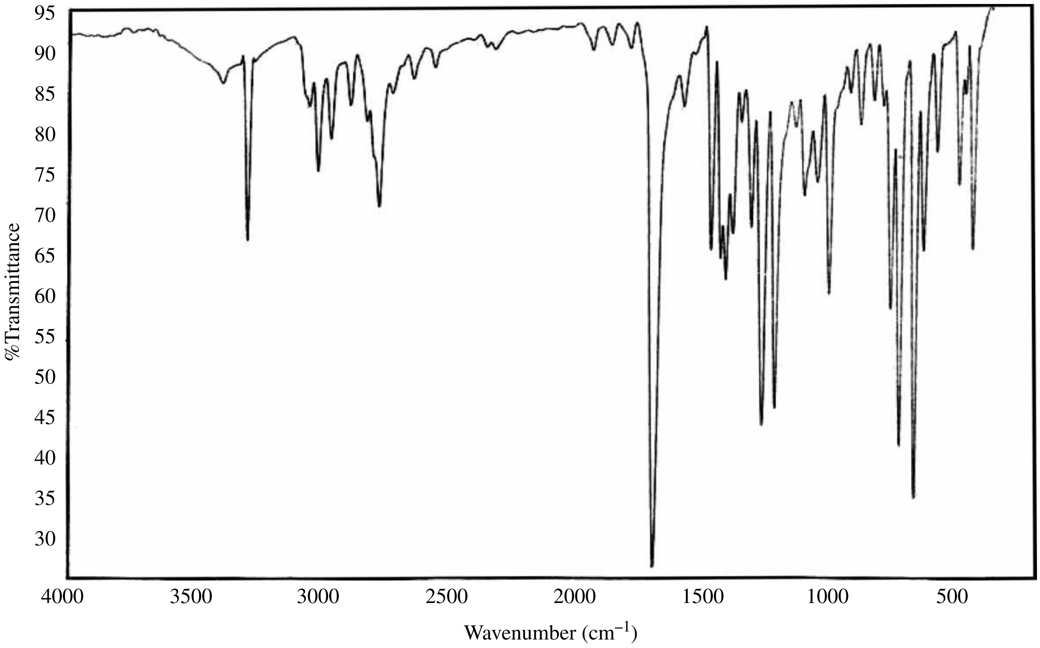

Figure 1. FT-IR spectrum of 4-PID.

6-311+G(3df,2p) and 6-311++G(d,p) basis set (referred as large basis set).

2. Experimental details

The compound 4-PID in the yellow liquid form was obtained from Department of Chemistry, Annamalai University. The FT-Raman spectrum of 4-PID has been recorded using 1064 nm line of Nd: YAG laser as excitation wavelength in the region 50–3500 cm^{-1} on a Thermo Electron Corporation model Nexus 670 spectrophotometer equipped with FT-Raman module accessory. The FTIR spectrum of this compound was recorded in the range of 400–4000 cm^{-1} on Nexus 670 spectrophotometer using neat technique. The spectrum was recorded at room temperature, with a scanning speed of 30 cm^{-1} min^{-1} and a spectral resolution of 4.0 cm^{-1}. The observed experimental FT-IR and FT-Raman spectra are shown in Figures 1 and 2. The theoretically predicted IR and Raman spectra at HF and B3LYP levels of calculations are shown

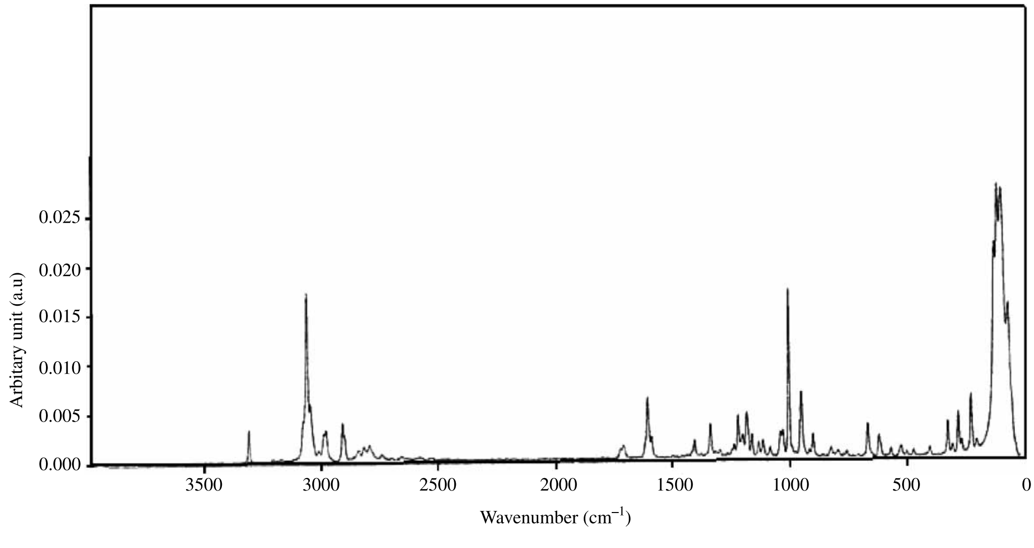

Figure 2. FT-Raman spectrum of 4-PID.

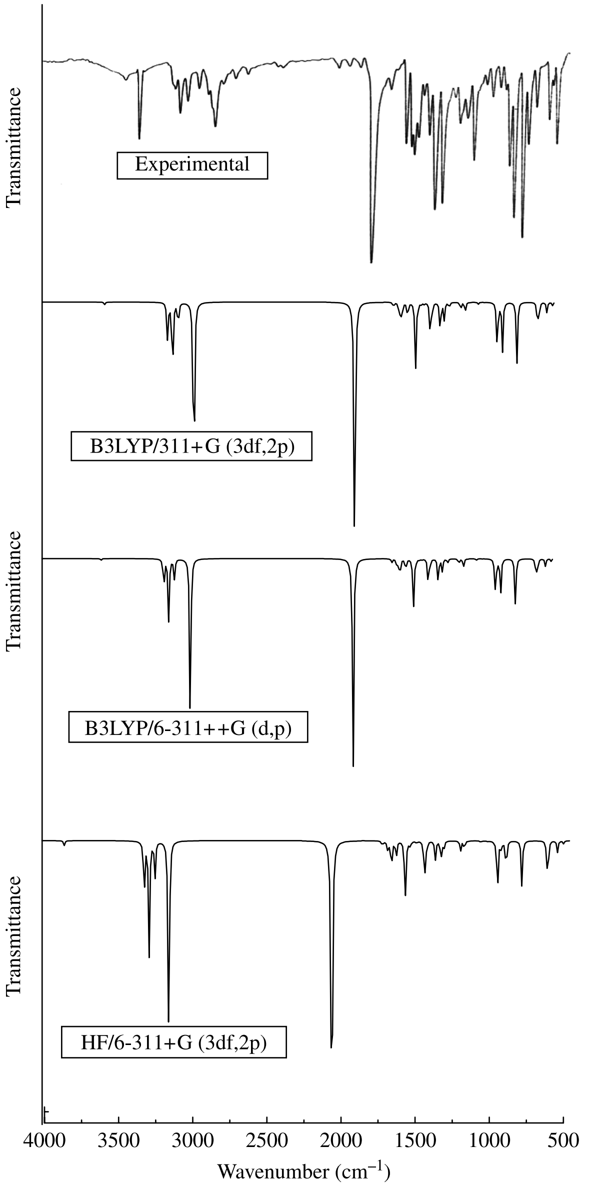

Figure 3. Comparison of observed and calculated infrared spectra of 4-PID.

in Figures 3 and 4. The spectral measurements were carried out at the Central Electro Chemical Research Institute (CECRI) Karaikudi, India.

3. Computational details

The entire calculations were performed at HF and DFT levels on a Pentium IV/3.02 GHz personal computer using Gaussian 03W [18] program package, invoking gradient geometry optimisation [19]. The initial geometry generated from standard geometrical parameters was minimised without any constraint in the potential energy surface at HF level, adopting the standard 6-311+ +G(d,p) basis set.

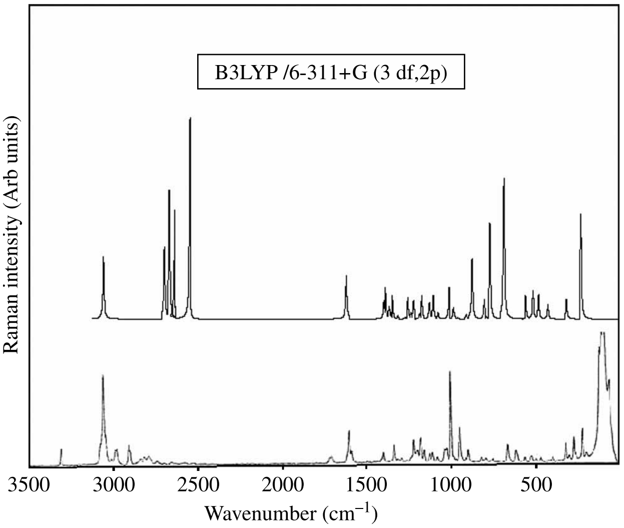

Figure 4. Comparison of experimental (below) and computed B3LYP/6-31+G(3df,2p)(top) FT-Raman spectrum of 4-PID.

This geometry was then re-optimised again at DFT level, using 6-311++G(d,p) and 6-311+G(3df,2p) basis sets for better description of polar bonds of C=O, NH and CH_2 groups. The optimised structural parameters were used in the vibrational frequency calculations at the HF and DFT levels to characterise all stationary points as minima. Three sets of vibrational frequencies for these species are calculated with HF/6-311+G(3df,2p), B3LYP/6-311+G(3df,2p) and B3LYP/6-311++G(d,p) methods and then scaled by 0.8992, 0.9945 and 0.9668, respectively [20]. By combining the results of the GAUSSVIEW program [21] with the symmetry considerations along with available related molecules, vibrational frequency assignments were made with a high degree of accuracy.

3.1 Prediction of Raman intensities

The Raman activities (S_i) calculated with the Gaussian 03 program converted to relative Raman intensities (I_i) using the following relationship derived from the intensity theory of Raman scattering [22,23].

$$I_i = \frac{f(\nu_o - \nu_i)^4 S_i}{\nu_i[1 - \exp(-hc\upsilon_i/kt)]},$$

where ν_o is the exciting frequency in cm^{-1}, ν_i is the vibrational wave number of the ith normal mode, h, c and k are the fundamental constants and f is a suitably chosen common normalisation factor for all peak intensities. For simulation, the calculated FT-Raman spectra have been plotted using pure Lorentizian band shape with a bandwidth of full width and half maximum (FWHM) of $10\,cm^{-1}$ as shown in Figure 4.

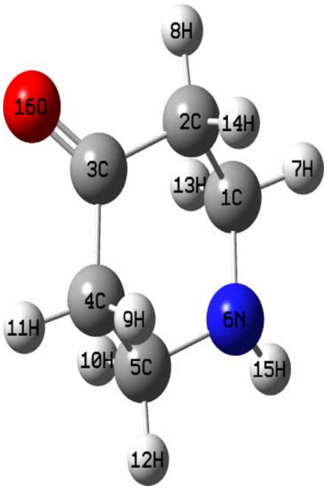

Figure 5. Atomic numbering system of 4-PID.

4. Results and discussion

4.1 Geometrical structure

The optimised geometric parameters (bond lengths and angles) by HF and B3LYP with 6-311+G(3df,2p) and 6-311+G(3df,2p), 6-311++G(d,p) basis sets are listed in Table S1 (as supplementary data) in accordance with the atom numbering scheme given in Figure 5. Since the crystal structure of the title compound is not available till now, the optimised structure can only be compared with other similar systems for which crystal structures have been solved. Therefore optimised geometrical parameters of 4-PIP are compared to those of 1-methyl-4-PID [17]. As discussed in the literature, it is well known that the HF method underestimates bond lengths and the B3LYP method predicts geometrical parameters, which are much closer to experimental data. Because of these reasons, we take into account B3LYP/6-311 + G(3df,2p) level for geometric parameters of 4-PIP in the present discussion. Krishnakumar et al. [17] gave only representative bond distances and bond angles, for 1-methyl-4-PID using 6-311G(d,p) basis set. In that study, the C—N—C bond angles are slightly shorter than the C—C—C or N—C—C bond angles while the C—N bond distances are predicted to be slightly shorter than C—C bond distances. Our data are consistent with these observations which can be seen from Table S1 (supplementary data). Generally, this type of compounds shows a twist nature (chair conformation) for their structure [24].

4.2 Vibrational analysis

In order to obtain the spectroscopic signature of 4-PID molecule, we performed a frequency calculation analysis. Calculations were made for a free molecule in vacuum, while experiments were performed for liquid samples and so disagreements between the calculated and observed vibrational wave numbers can be found, and some frequencies are calculated; however these frequencies are not observed in the FT-IR and Raman spectra. The observed deviations between the theory and experiment could be a consequence of the general tendency of the quantum chemical methods to overestimate the force constants at the exact equilibrium geometry [25], anharmonicity and structural features of the liquid state. The calculated IR spectra are shown in Figure 3 for comparative purposes, where the calculated intensity is plotted against the harmonic vibrational frequencies. The experimental wave numbers are tabulated in Table 1 together with the calculated wave number of studied molecule. In chair conformations of 4-PID, they show C_s symmetry. The 42 normal modes of 4-PID are distributed amongst the symmetry species as $\Gamma_{3N-6} = 29A'$ (in plane) $+ 13A''$ (out of plane) in agreement with C_s symmetry. The calculated vibrations are scaled and the symmetry species of all the vibrations are written in the first column of the table. As we said before, the vibrations in-plane belong to the A' species and the others out-of-plane belong to the A'' species. This is indeed what we have observed by means of the visual inspection of all the vibrations. All the vibrational modes are IR and Raman active.

4.3 Methylene group vibrations

For the assignment of CH_2 group frequencies, basically six fundamentals can be associated to each CH_2 group namely, CH_2 sy, symmetric stretch; CH_2 asy, asymmetric stretch; CH_2 sciss, scissoring and CH_2 rock, rocking modes which belong to polarised in-plane (A') vibrations. In addition to that, CH_2 wag, wagging and CH_2 twist, twisting modes of CH_2 group would be expected to be depolarised for out-of-plane (A'') symmetry species.

The C—H stretching of the methylene groups is at lower frequencies than those of the aromatic C—H ring stretching. The asymmetric CH_2 stretching vibrations are generally observed in the region of 3000–2900 cm^{-1}, while the CH_2 symmetric stretch will appear between 2900 and 2800 cm^{-1} [26,27]. The CH_2 asymmetric stretching vibrations were observed in IR and Raman spectra at 3030, 2983 and 3056 and 2980, respectively, for 4-PID. We calculated the asymmetric CH_2 stretching of the methylene group at the 2980, 2979, 2947 and 2945 cm^{-1} by B3LYP/6-311+G(3df, 2p) method. We calculated the symmetric stretching of CH_2 group at the 2908, 2903, 2802 and 2800 cm^{-1} by B3LYP/6-311+G(3df,2p). The experimental observations at 2907 in FT-Raman and 2890 and 2790 cm^{-1} in FT-IR exactly correlate with scaled values. In the present assignment the CH_2 bending modes follow, in decreasing wave number, the general order CH_2 deformation $>$ CH_2 wagg $>$ CH_2 twist $>$ CH_2 rock. Since the bending modes involving the hydrogen atom

Table 1. Comparison of the observed (FT-IR and FT-Raman) and calculated vibrational frequencies of 4-PID.

Species	RHF-6-311 + G(3df,2p)			B3LYP/6-311++G(d,p)			RB3LYP/6-311 + G(3df,2p)			Experimental		Vibrational assignments
	Scaled freq	I^{Infrared}	S^{Raman}	Scaled freq	I^{Infrared}	S^{Raman}	Scaled freq	I^{Infrared}	S^{Raman}	FT-IR	FT-Raman	
A''	96	2	0	92	2	0	91	2	0		98	C═O torsion + ring torsion
A'	193	0	0	196	1	0	191	1	0		229w	CH_2ipb
A'	321	0	0	327	1	0	319	1	0		327w	CN opb + CH_2 torsion
A'	386	1	0	392	1	0	384	1	0			CCC opb
A'	423	3	0	432	3	1	422	3	1			CNC ipb
A''	478	4	1	484	2	1	474	2	1	470s		C═O opb
A'	487	6	0	495	8	0	485	8	0	524m		NCC ipb
A''	638	12	4	638	20	4	624	19	4	663w	665w	CCC opb + NH opb
A'	733	8	6	739	16	3	722	16	4	697s		CCC ipb
A'	762	2	0	765	4	0	748	4	0	756s		C═O ipb
A''	785	15	0	778	12	1	760	11	1	790m		NH opb
A''	844	0	4	864	0	3	845	0	3			CCC opb
A''	886	0	0	906	1	0	885	1	0	913w		CCC opb
A'	958	0	0	965	0	0	946	0	0		949m	CCC ipb
A'	985	2	2	995	3	1	974	3	1			CCC ipb
A'	1009	3	2	1026	2	2	1004	2	2	1032m	1002s	ρCH_2
A'	1109	2	1	1102	1	1	1081	1	0			ρCH_2
A'	1110	1	1	1108	0	1	1082	0	0	1078w		ρCH_2
A'	1127	5	2	1139	5	2	1115	6	2			ρCH_2
A''	1160	5	1	1168	10	2	1141	10	1	1129w		tCH_2
A''	1211	2	2	1223	2	2	1195	2	2		1181w	tCH_2
A''	1225	10	0	1236	11	0	1208	11	0			tCH_2
A''	1273	1	2	1280	0	2	1251	0	2	1242s		tCH_2
A''	1310	1	0	1300	0	1	1269	0	1		1271w	ωCH_2
A''	1326	1	1	1322	2	2	1292	2	2			ωCH_2
A''	1342	17	0	1338	20	0	1308	20	0	1292s		ωCH_2
A''	1396	4	0	1391	5	1	1361	5	0	1335w	1336w	ωCH_2
A'	1422	5	3	1428	5	3	1399	5	3			δCH_2
A'	1432	3	1	1439	4	1	1410	4	1			δCH_2
A'	1448	2	3	1453	2	2	1421	2	1	1434w		βNH
A'	1471	0	2	1476	0	4	1447	0	4	1456w		δCH_2
A'	1480	1	2	1486	2	2	1457	2	2	1493w		βCH_2
A'	1785	100	8	1707	100	6	1718	100	7	1721vs	1720vw	νC═O
A'	2764	7	6	2794	12	10	2800	12	10			ν_{sy}CH in CH_2
A'	2769	43	100	2796	55	100	2802	54	100	2790w		ν_{sy}CH in CH_2
A'	2846	0	7	2898	0	7	2903	0	7	2890w		ν_{sy}CH in CH_2
A'	2852	9	62	2902	8	58	2908	8	59		2907w	ν_{sy}CH in CH_2
A'	2886	20	37	2940	18	34	2945	18	35			ν_{asy}CH in CH_2
A'	2888	9	84	2941	8	68	2947	8	73			ν_{asy}CH in CH_2
A'	2915	9	28	2973	8	27	2979	8	27	2983w	2980w	ν_{asy}CH in CH_2

Table 1 – *continued*

Species	RHF-6-311 + G(3df,2p)			B3LYP/6-311++G(d,p)			RB3LYP/6-311 + G(3df,2p)			Experimental		Vibrational assignments
	Scaled freq	I^{Infrared}	S^{Raman}	Scaled freq	I^{Infrared}	S^{Raman}	Scaled freq	I^{Infrared}	S^{Raman}	FT-IR	FT-Raman	
A'	2917	6	49	2974	4	39	2980	4	41	3030w	3056s	ν_{asy}CH in CH_2
A'	3398	1	53	3392	1	55	3403	1	56	3306m	3306w	νNH
Total energy (a.u.)	−324.0006			−326.0151			−326.0356					
Dipole moment (Debye)	3.56			3.49			3.44					

ν, stretching; ν_s, sym. stretching; ν_{as}, asym. stretching; β, in-plane-bending; γ, out-of-plane bending; ω, wagging; ρ, rocking; t, twisting; δ, scissoring [frequency (cm^{-1})], I^{Infrared} (km/mol), IR intensities; S^{Raman} (Å^{-4} amu^{-1}), Raman scattering activities.

attached to the central carbon atom falls into the 1450–875 cm^{-1} range, there is extensive vibrational coupling of these modes with CH_2 deformations, particularly with the CH_2 twist. It is notable that both δCH_2 and ρCH_2 were sensitive to the molecular conformation. For cyclohexane, the CH_2 scissoring mode has been assigned to the medium intensity IR band at about 1450 cm^{-1} [28]. We have predicted [29] in 3-aminobenzylalcohol that the medium intensity FT-IR band at 1464 cm^{-1} and FT-Raman band at 1465 cm^{-1} have been assigned to the CH_2 scissoring vibration. This band probably obscures the C—C vibration of phenyl mode. In our title molecule the scaled vibrational frequencies 1457, 1447, 1421 and 1410 cm^{-1} by B3LYP/6-311+G(3df,2p) method exactly coincide with FT-IR experimental observation of 1493, 1456 and 1434 cm^{-1}. The CH_2 twists are observed to be strong FT-IR band at 1242 cm^{-1}, weak FT-IR band at 1129 cm^{-1} and the same vibration in FT-Raman is also observed as weak bands at 1181 cm^{-1}. The CH_2 twist of 4-PID is predicted at 1251, 1208, 1195 and 1141 cm^{-1} by B3LYP/6-311+G(3df,2p) method which exactly correlates with experimental observations. In the infrared spectrum of 4-PID a weak band at 1335 with another band of almost equal intensity at 1336 and 1271 cm^{-1} and a strong band at 1292 cm^{-1} is assigned to CH_2 waggings vibrations. From B3LYP/6-311+G(3df,2p) calculations, the CH_2 waggings predicted to be at 1361,1308, 1292 and 1269 cm^{-1} are in excellent agreement with the experimental observation. The rocking modes that were observed at 1078, 1032 and 1002 cm^{-1} in the infrared and Raman spectra, respectively, also exactly correlate with scaled values by B3LYP/6-311+G(3df,2p) method in the range of 1115–1004 cm^{-1}.

4.4 C═O vibrations

The carbonyl stretching frequency has been most extensively studied by infrared spectroscopy [30]. This multiple bonded group is highly polar and therefore gives rise to an intense infrared absorption band. In the present study the carbonyl-stretching vibrations are found in the region of 1780–1700 cm^{-1} [31]. The sharp intense band in the IR spectrum at 1721 cm^{-1} can be assigned to C3═O16 stretching vibration, which is also observed in Raman at 1721 cm^{-1} as a very weak band. The results of computation give the frequencies of these modes at 1707 and 1718 cm^{-1} by B3LYP method with a very strong IR predicted intensity and low Raman scattering activity show excellent agreement with our experimental data. Krishnakumar et al. [17] predicted the same vibration at 1680 cm^{-1} by B3LYP/6-311+G(d,p) method in 1-methyl–4-PID molecule. The C═O bending, wagging and torsion vibrations are observed as intense bands in the IR spectrum in the expected regions [32] at 756, 470 and

98 cm^{-1}, respectively. The bands are separately identified by the computational results.

4.5 N—H vibration

Primary aliphatic amines absorb in the region of 3450–3250 cm^{-1} in solids or liquids and they have broad and medium intensity. In solid and liquid phases, a band of medium intensity is observed in the range of 3400–3300 cm^{-1} for secondary aromatic amines. The vibrational bands due to the N—H stretching are sharp and weak than those of O—H stretching vibrations by virtue of which they can be easily identified [33]. By observing the position of the band in the proper region, the vibrational band present at 3306 cm^{-1} as a medium band in FT-IR and a weak band at 3306 cm^{-1} in FT-Raman is assigned as N6—H15 stretching vibration. It was calculated it to be 3398, 3392 and 3406 cm^{-1} (HF/6-311+G(3df,2p)), B3LYP/6-311++G(d,p) and B3LYP/6-311+G(3df,2p), respectively. The scaled value of N6—H15 stretching vibration is deviating ~90–100 cm^{-1} from the experimental observation. Usually, primary amides and secondary amides show a band or bands in the region of 1515–1350 cm^{-1} primarily due to N—H bending [34]. In the present work, the weak band appears at 1434 in FT-IR and is assigned to N6–H15 in plane bending mode. The theoretically scaled value at 1421 cm^{-1} by B3LYP/6-311+G(3df,2p) is in excellent agreement with experimental observations.

4.6 Ring vibrations

Many ring modes are affected by the substitutions in the ring of 4-PID. In the present study, the bands predicted at 974, 946, 722 and 885, 845, 624 cm^{-1} have been designated to ring in-plane and out-of-plane bending modes, respectively, by careful consideration of their quantitative descriptions. The experimental observations at 913, 697 also coincide with theoretically predicted values.

4.7 HOMO–LUMO analysis

Many organic molecules, containing conjugated π electrons are characterised by large values of molecular first hyper-polarisabilities, were analysed by means of vibrational spectroscopy [35,36]. In most 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 transfer from the donor to accepter group through a single–double bond conjugated path can induce large variations of both the molecular dipole moment and the molecular polarisability, making IR and Raman activity strong at the same time. The experimental spectroscopic behaviour described above is well accounted for by *ab initio* calculations in π conjugated systems that predict exceptionally large Raman and infrared intensities for the same normal modes [36]. It is also observed in our title molecule that the bands in FT-IR spectrum have their counterparts in the Raman which shows that the relative intensities in IR and Raman spectra are comparable and the result from the electron cloud movement through π conjugated frame work from electron donor to electron acceptor groups. The analysis of the wave function indicates that the electron absorption corresponds 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). The LUMO of π nature (i.e. piperidine ring) is delocalised over the whole C—C bond. By contrast, the HOMO is located over N and the lower part of the ring, consequently the HOMO → LUMO transition implies an electron density transfer to C=O and the upper part of the ring. Moreover, these orbitals significantly overlap in their position for 4-PID. The atomic orbital compositions of the frontier molecular orbital are sketched in Figure 6.

The HOMO–LUMO energy gap of 4-PID was calculated at the B3LYP/6-311+ G(3df,2p) level and is shown in Table 2, which reveals that the energy gap reflect

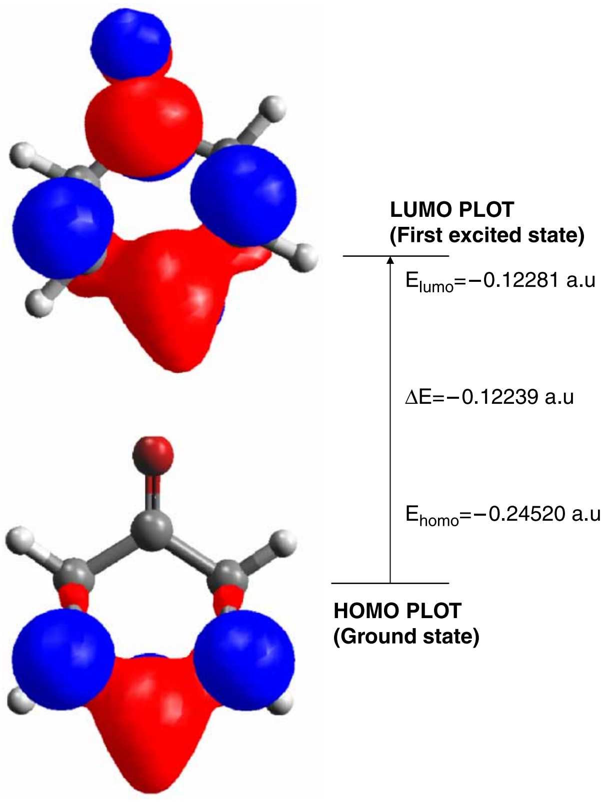

Figure 6. Electron distribution of HOMO and LUMO energy levels for 4-PID.

Table 2. HOMO–LUMO energy value calculated by HF and DFT methods.

Parameters (a.u.)	RHF/6-311+ G(3dfd,2p)	B3LYP/6-311 ++G(d,p)	B3LYP/6-311+ G(3df,2p)
HOMO	−0.41934	−0.24428	−0.24520
LUMO	−0.38637	−0.12435	−0.12281
HOMO–LUMO	−0.03297	−0.11993	−0.12239

the chemical activity of the molecule. LUMO as an electron acceptor represents the ability to obtain an electron and HOMO represents the ability to donate an electron.

$$\text{HOMO energy} = -0.24520\,\text{a.u.}$$

$$\text{LUMO energy} = -0.12281\,\text{a.u.}$$

$$\text{HOMO–LUMO energy gap} = -0.12239\,\text{a.u.}$$

The calculated self-consistent field (SCF) energy of 4-PID is −326.0356 a.u. Moreover the lower HOMO and LUMO energy gap explains the eventual charge transfer interactions taking place within the molecule.

5. Conclusions

Comparison of the observed fundamental frequencies of 4-PID and the results calculated by density functional B3LYP and HF methods indicate that B3LYP is superior to the scaled HF approach for molecular vibrational problems. On the basis of calculated results, assignments of the fundamental vibrational frequencies have been proposed. The good agreement between frequencies calculated by B3LYP/6-311+G(3df,2p) and experimental results indicate that the density functional methods are reliable and provide valuable information in understanding the vibrational spectra of the title molecule. The optimised geometry parameters calculated at HF/6-311+G(3df,2p) is slightly shorter than those calculated at B3LYP/6-311+G(3df,2p) level and the B3LYP/6-311+G(3df,2p) calculated values coincide well compared with the available experimental data on the whole. The calculated HOMO and LUMO energies show that charge transfer occurs within the molecule. In general the IR and Raman spectra are used in conjunction with other forms of spectroscopy and chemical analyses to determine the structures of complicated organic molecules.

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