

Molecular Structure, Vibrational Spectroscopic, First Order Hyperpolarizability and Homo–Lumo Studies of 1-Aminopiperidine Using *Ab Initio* Hf and DFT Calculations

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Abstract

The molecular vibrations Of 1-Aminopiperidine has been investigated at room temperature by Fourier transform infrared FT-IR and FT-Raman spectroscopies. The spectra of the molecule have been recorded in the regions 4000-400 cm⁻¹ and 3500-50 cm⁻¹ respectively. Theoretical information on the optimized geometry, harmonic vibrational frequencies, infrared and Raman intensities were obtained by means of ab initio Hartree–Fock (HF) and Density functional theory (DFT) using 6-311+G(d,p) basis set. The vibrational frequencies which were determined experimentally from the spectral data are compared with those obtained theoretically from ab initio and DFT calculations. A close agreement achieved between the observed and calculated frequencies by refinement of the scale factors. The HOMO-LUMO and Thermodynamic properties like entropy, heat capacity, zero point energy have been calculated for the molecule.

Key Words: FTIR; FT-Raman; NLO, HOMO-LUMO

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1. 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 are also reported to possess analgesic anti-inflammatory central nervous system local anesthetic anticancer and antimicrobial activity. Piperidine nucleus is also found in drugs as raloxifene, minoxidil and as a raw material for preparing epoxy resins, corrosion inhibitors and antioxidant. The vibrational studies of piperidine and theoretical studies of density functional calculations are also reported [1-20]. The literature survey also reveals that no theoretical calculations or detailed vibrational infrared and Raman spectral analysis have been performed on 1-aminopiperidine (1-AP) molecule so far. A systematic study on the vibrational spectra and structure will aid in understanding the vibrational modes of 1-AP. In the present investigation, the vibrational wave numbers, geometrical parameters, modes of vibrations, minimum energy, also provide information about electronic effects of 1-AP are investigated by using *ab initio* HF and DFT/B3LYP methods with 6-31+G(d,p) basis set. Specific scale factors are also used and employed in the predicted frequencies. The electronic dipole moment (μ) and the first hyperpolarizability (β) value of the investigate molecule computed show that the 1-AP 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.

2. EXPERIMENTAL PROCEDURE

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

3. METHODS OF COMPUTATION

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 are carried out for 1-AP with GAUSSIAN 09W program package [21]. Initial geometry generated from the standard geometrical parameters is 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 is 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 are 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 are 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) are 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. Normal coordinate analysis is carried out for the 1-AP to provide a complete assignment of fundamental frequencies. The theoretically calculated force fields are transformed to this set of vibrational coordinates and used in all subsequent calculations.

4. RESULTS AND DISCUSSION

4.1. Molecular geometry

The optimized molecular structure of 1-AP along with numbering of atoms is shown in Fig. 1. The optimized geometrical parameters of 1-AP obtained by DFT-B3LYP/6-311++G(d,p) and HF/6-311++G(d,p) levels are listed in Table 1. It is observed that the various bond lengths are found to be almost same at HF/6-311++G(d,p) and B3LYP/6-311++G(d,p) levels. However, the B3LYP/6-311++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. The optimized molecular structure of 1-AP reveals that the two methyl groups are in planar with the heterocyclic ring. Inclusion of CH₃ group and NH atoms known for its strong electron-withdrawing nature. It is expected to increase a contribution of the resonance structure, in which the electronic charge is concentrated at this site..

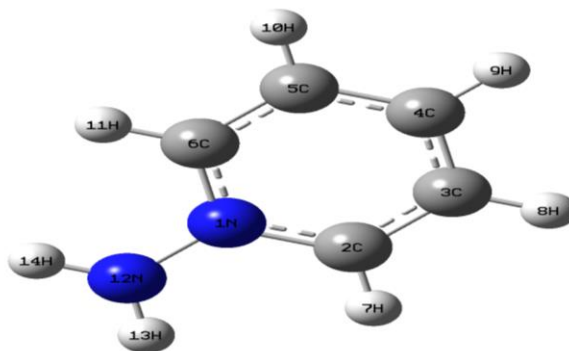


Fig. 1: Molecular structure of 1-aminopiperidine

5. FIRST HYPERPOLARIZABILITY

The first hyperpolarizability (β_0) of these novel molecular system and the related properties (β_0 , α_0) of 1-AP have been calculated 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 $3 \times 3 \times 3$ matrix. It can be given in the lower tetrahedral. The components of β are defined as the

coefficients in the Taylor series expansion of the energy in the external electric field. When the external electric field is weak and homogenous, this expansion becomes,

$$E = E^{\circ} - \mu_{\alpha} F_{\alpha} - \frac{1}{2} \alpha_{\alpha\beta} F_{\alpha} F_{\beta} - \frac{1}{6} \beta_{\alpha\beta\gamma} F_{\alpha} F_{\beta} F_{\gamma} + \dots \quad \dots (1)$$

where E° is the energy of the unperturbed molecules, F_{α} the field at the origin and μ_{α} , $\mu_{\alpha\beta}$ and $\beta_{\alpha\beta\gamma}$ are the components of dipole moment, polarizability and the first hyperpolarizabilities, respectively. The total static dipole moment μ , the mean polarizability α_0 , the anisotropy of the polarizability β_0 , using the x, y, z components they are defined as follows.

$$\mu = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2}$$

$$\alpha_0 = \frac{\alpha_{xx} + \alpha_{yy} + \alpha_{zz}}{3}$$

$$\alpha = 2^{-1/2} [(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2 + 6\alpha_{xx}^2]^{1/2}$$

$$\beta_0 = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2}$$

and

$$\beta_x = \beta_{xxx} + \beta_{xyy} + \beta_{xzz}$$

$$\beta_y = \beta_{yyy} + \beta_{xxy} + \beta_{yzz}$$

$$\beta_z = \beta_{zzz} + \beta_{xxz} + \beta_{yyz}$$

The total molecular dipole moment (μ) and mean first hyperpolarizability (β) are 1.6809 Debye and 0.8906×10^{-30} esu. The total dipole moment and the first hyperpolarizability of the title compound are many times more than those of urea (μ and β of urea are 1.3732 Debye and 0.3728×10^{-30} esu).

6. HOMO-LUMO ANALYSIS

This electronic 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) [28-29]. 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 amino group. Moreover, these orbital's significantly overlap in their position for 1-AP is shown in Fig. 2. The HOMO-LUMO energy gap of 1-AP is 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 π -conjugated path. The strong charge transfer interaction through π -conjugated bridge results in substantial ground state Donor-Acceptor (DA) mixing and the appearance of a charge transfer band in the electron absorption spectrum.

For 1-AP,

$$\text{HOMO energy} = -0.2401 \text{ a.u.}$$

$$\text{LUMO energy} = -0.3885 \text{ a.u.}$$

$$\text{HOMO-LUMO energy gap} = 0.14835 \text{ a.u.}$$

The HOMO and LUMO energy gap explains the fact that eventual charge transfer interaction is taking place within the molecule.

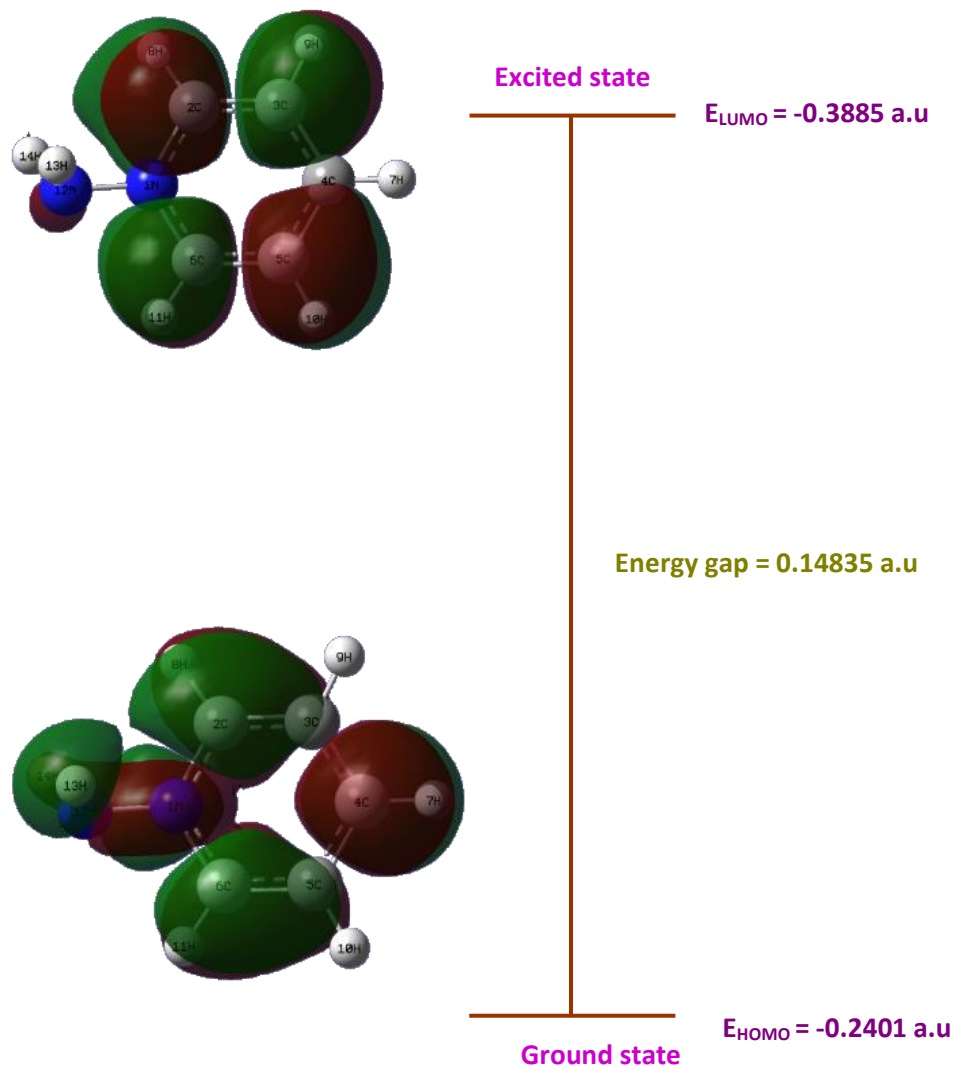


Fig. 2: HOMO-LUMO plot of 1-aminopiperidine

7. VIBRATIONAL SPECTRA

From the structural point of view the 1-AP is assumed to have C_s point group symmetry. The 36 fundamental modes of vibrations arising for 1-AP is distributed amongst the symmetry species as.

$$\overline{3N - 6} = 25 \text{ A}' (\text{in-plane}) + 11 \text{ A}'' (\text{out-of-plane})$$

The A' and A'' species represent the in-plane and out-of-plane vibrations, respectively. The observed FTIR and FT-Raman spectra of 1-AP are shown in Figs. 3 and 4, respectively. The detailed vibrational assignments of fundamental modes of 1-AP along with the calculated IR and Raman frequencies and normal mode descriptions (characterize by TED) are reported in Table 2. The vibrational analysis obtained for 1-AP with the unscaled HF and B3LYP/6-

311++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 [30]. 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.

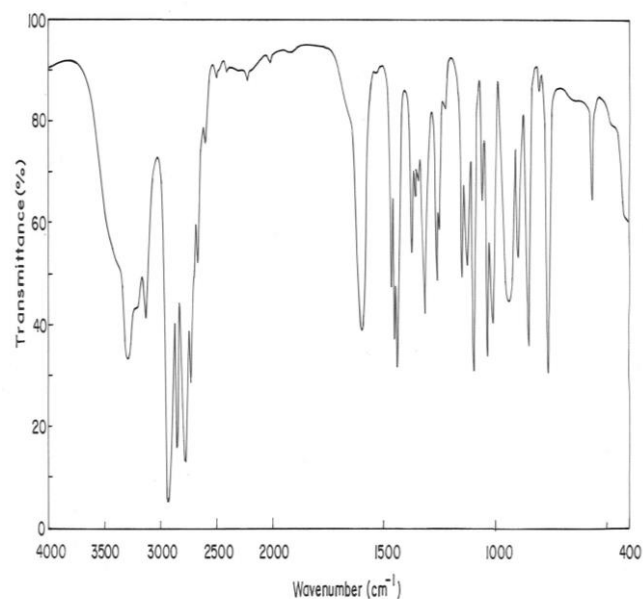


Fig. 3: FTIR spectrum of 1-aminopiperidine

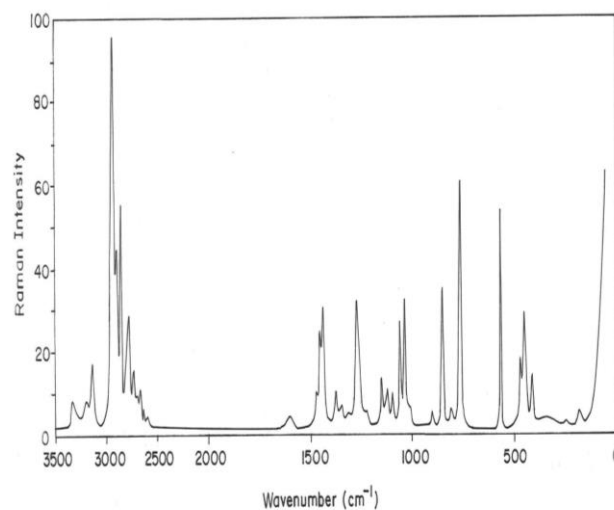


Fig. 4: FT-Raman spectrum of 1-aminopiperidine

C-H vibrations

The hetero aromatic structure shows the presence of C-H stretching vibration in the region 3100-3000 cm^{-1} . The experimental frequencies observed at 3100, 2953 cm^{-1} in FTIR and 3180, 3150, 3000 cm^{-1} in FT-Raman spectrum are assigned C-H stretching vibrations of 1-AP. The C-H in-plane bending vibrations appear in the range of 1390-990 cm^{-1} in the substituted hetero structure and the out-of-plane bending vibrations occurs in the frequency range of 900 - 675 cm^{-1} [30]. Accordingly, the IR frequencies assigned to C-H in-plane bending vibrations are observed at 1210, 1170, 1150 cm^{-1} and in Raman frequency observed at 1230, 1169, 1130 cm^{-1} for 1-AP. The C-H out-of-plane bending vibrations are observed at 770, 570 cm^{-1} in IR and in Raman 820, 680, 490 cm^{-1} for 1-AP. The slight deviation in low frequency bands are due to the interaction between NH_2 and C-H out-of-plane bending frequencies, which is also confirmed by TED output.

C-C vibrations

The C-C stretching vibrations of which the three with highest wave numbers occurring near 1650 - 1400 cm^{-1} are good group vibrations [31-32]. With heavy substituents, the bonds tend to shift to somewhat lower wavenumbers and greater the number of substituents on the ring, broader the absorption regions. As predicted in the earlier references, the present investigation, the C-C stretching vibrations observed at 1480, 1420, 1380, 1360 cm^{-1} in FT-IR and 0, 1423, 1385, 1358 cm^{-1} in FT-Raman for 1-AP. Most of the ring vibrational modes are affected by the substitutions in the hetero aromatic ring of 1-AP. In the present investigation, the bands observed at 1080 cm^{-1} in FTIR and in Raman 1080, 1030, 860 cm^{-1} for 1-AP have been designated to ring in-plane bending modes by careful consideration of their quantitative descriptions. The ring out-of-plane bending modes of 1-AP is also listed in Tables 2.

C-N vibrations

In hetero aromatic compounds, the C-N stretching vibration usually lies in the region 1400-1200 cm^{-1} . The identification of C-N stretching frequencies is a rather difficult task. Since the mixing of vibrations is possible in this region [31]. In this study, the C-N stretching vibrations of 1-AP are found at 1310, 1270 cm^{-1} in the FTIR spectrum and at 1270 cm^{-1} in the FT-Raman spectrum of 1-AP. The C-N bending vibrations and deformations are in close agreement with literature value and also listed in Table 2.

NH_2 vibrations

The 1-AP molecule under consideration posses NH_2 group and hence six internal modes of vibration are possible such as symmetric stretching, asymmetric stretching, scissoring, rocking, wagging and torsional mode. The frequency of asymmetric vibration is higher than that of symmetric one. The frequencies of amino group in the region 3500 - 3300 cm^{-1} for NH stretching, 1700 - 1600 cm^{-1} for scissoring and 1150 - 900 cm^{-1} for rocking deformation. In the present investigation, the asymmetric and symmetric modes of NH_2 group are assigned at 3350 cm^{-1} (FT-Raman) and 3300 cm^{-1} (FTIR) respectively. The band observed at 1620 cm^{-1} in FT-Raman spectrum is assigned to NH_2 scissoring mode. The rocking, wagging, twisting deformation vibrations of NH_2 contribute to several normal modes in the low frequency region. The band observed at 1100 cm^{-1} in both FTIR and FT-Raman is assigned to NH_2

rocking vibrations and the FT-Raman band observed at 750 cm^{-1} is assigned to NH_2 wagging mode, and the band observed at 180 cm^{-1} in Raman is assigned to NH_2 twisting modes [34].

8. OTHER MOLECULAR PROPERTIES

Several calculated thermodynamical parameters, rotational constants, rotational temperature, vibrational temperature and dipole moment have been presented in Table 3. The zero-point vibrational energies, the entropy and the molar capacity at constant volume are calculated. The variation in the zero-point vibration energies seems to be insignificant. The changes in the total entropy of 1-AP at room temperature at different methods are only marginal [35]. The dipole moment of the molecule is also calculated by *ab initio* HF and DFT/B3LYP using 6-311++G(d,p) basis set.

9. CONCLUSION

Based on the *ab initio* HF and density functional theory calculations with HF/B3LYP/6-31+G(d,p), levels, complete vibrational properties of 1-aminopiperidine have been investigated by FT-IR and FT-Raman spectroscopy. A good correlation is found between the computed and experimental wavenumbers. The calculated first hyperpolarizability is found to be 0.10945×10^{-30} esu for 1-AP. HOMO and LUMO energy gap explains the eventual charge transfer interactions taking place within the molecule. This study demonstrates that scaled calculations are powerful approach for understanding the vibrational spectra of organic compounds

Table 1: Optimized geometrical parameters of 1-aminopiperidine obtained by HF and B3LYP methods with 6-311++G(d,p) basis set

Bond Length	Value (Å)		Bond Angle	Value (°)		Dihedral Angle	Value (°)	
	HF/ 6- 311++G(d,p)	B3LYP/ 6- 311++G(d,p)		HF/ 6- 311++G(d,p)	B3LYP/ 6- 311++G(d,p)		HF/ 6- 311++G(d,p)	B3LYP/ 6- 311++G(d,p)
N1-C2	1.4037	1.4092	C2-N1-C6	117.6363	118.603	C6-N1-C2-C3	8.1919	6.1289
N1-C6	1.4011	1.4008	C2-N1-N12	118.264	119.7603	C6-N1-C2-H8	-175.8855	-177.6048
N1-C12	1.3967	1.4137	C6-N1-N12	114.5637	115.5827	N12-N1-C2-C3	152.7063	157.5728
C2-C3	1.3709	1.3724	N1-C2-C3	121.4475	120.5371	N12-N1-C2-H8	-31.3712	-26.1609
C2-8H	1.0731	1.0832	N1-C2-H8	115.4106	115.4347	C2-N1-C6-C5	-8.2449	-6.2476
C3-C4	1.4151	1.4139	C3-C2-H8	123.0085	123.9141	C2-N1-C6-H11	174.3453	175.7095
C3-9H	1.0751	1.0861	C2-C3-C4	120.6121	121.246	N12-N1-C6-C5	-154.0392	-158.8555
C4-C5	1.4187	1.4226	C2-C3-H9	118.6017	118.0887	N12-N1-C6-H11	28.551	23.1016
C4-7H	1.0735	1.0829	C4-C3-H9	120.7862	120.6653	C2-N1-N12-H14	-47.6895	-51.0702
C5-C6	1.3673	1.3678	C3-C4-C5	117.5639	117.3207	C6-N1-N12-H13	74.1669	68.2023
C5-H10	1.0749	1.0855	C3-C4-H7	121.16	121.3145	C6-N1-N12-H14	97.8775	101.2004
C6-H11	1.0708	1.0817	C5-C4-H7	121.248	121.3398	N1-C2-C3-C4	-140.2661	-139.5271
N12-	1.0033	1.0237	C4-C5-C6	120.7881	121.1507	N1-C2-C3-H9	-3.3444	-2.3358

H13								
N12-H14	0.9988	1.0165	C4-C5-H10	120.6658	120.6988	H8-C2-C3-C4	176.683	177.5871
			C6-C5-H10	118.5457	118.1505	H8-C2=C3-H9	-178.952	-178.2722
			N1-C6-C5	121.4116	120.8351	C2-C3-C4-C5	1.0754	1.6507
			N1-C6-H11	114.6173	114.4329	C2-C3-C4-H7	-1.6494	-1.4014
			C5-C6-H11	123.9164	124.7002	H9-C3-C4-C5	-179.7456	-179.6068
			N1-N12-H13	111.2134	109.9995	H9-C3-C4-H7	178.3226	178.6777
			N1-N12-H14	109.7495	108.9663	C3-C4-C5C6	0.2264	0.4723
			H13-N12-H14	109.9267	108.8671	C3-C4-C5-H10	1.5975	1.3004
						H7-C4-C5-C6	-1781659	-178.7087
						H7-C4-C5-H10	179.692	179.5053
						C4-C5-C6-N1	-0.0715	-0.5038
						C4-C5-C6-N1	3.462	2.5686
						C4-C5-C6-H11	-179.3757	-179.5988
						H10-C5-C6-N1	-176.7696	-177.4225
						H10-C5-C6-H11	0.3927	0.4101

For numbering of atoms refer Fig1

Table 2: The observed (FTIR and FT-Raman) and calculated (Unscaled and Scaled) frequencies (cm^{-1}) and probable assignments (Characterized by TED) of 1-aminopiperidine using HF/6-311++G(d,p) and B3LYP/6-311++G(d,p) methods and basis set

Symmetry Species C_s	Observed Frequencies		Calculated Frequencies		Assignment with TED (%)
	FTIR	FT-Raman	B3LYP/ 6-311++G(d,p)	HF/ 6-311++G(d,p)	
A'	-	3350	3554	3831	vNH2 ass(100)
A'	3300	-	3399	3704	vNH2ss(9)
A'	-	3180	3252	3415	vCH(98)
A'	-	3150	3231	3385	vCH(98)
A'	3100	-	3226	3376	vCH(95)
A'	-	3000	3199	3358	vCH(96)
A'	2953	-	3192	3351	vCH(97)
A'	-	1620	1680	1825	vNH2sciss(86)
A'	1600	-	1646	1703	vNN(88)
A'	1480	1480	1533	1627	vCC(89)
A'	1420	1423	1464	1574	vCC(90)
A'	1380	1385	1374	1488	vCC(87)Rsymd(11)
A'	1360	1358	1348	1440	vCC(80)CC(15)
A'	1310	-	1327	1430	vCN(81)bCN(13)
A'	1270	1270	1300	1412	vCN(80)Rasymd(14)
A'	-	1230	1213	1323	bCH(74)CC(13)
A'	1210	-	120	1265	bCH(71)bCH(19)
A'	1170	1169	1105	1180	bCH(78)Rasymd(19)
A'	-	1130	1087	1134	bCH(76)Rtrigd(13)bCH(10)

A'	1150	-	1022	1089	bCH(77)bCC(13)
A'	1100	1100	1001	1038	NH2rock(69)
A'	1080	1080	931	991	Rsymd(86)bNN(11)
A'	-	1030	926	973	Rtrigd(82)bCH(11)
A'	1000	-	899	965	bNN(71)bCH(13)
A'	-	860	782	833	Rasymd(60)
A''	-	820	750	782	ω CH(56)Rasymd(30)
A''	770	-	690	748	ω CH(59)Rsymd(27)
A''	-	750	643	682	NH2wag(11)tRsymd(10)
A''	-	680	634	67	ω CH(61) ω NN(20)
A''	570	-	618	619	ω CH(60)
A''	-	490	509	542	ω CH(62)
A''	-	470	454	475	tRsym(51)
A''	-	410	396	421	tRtrig(57)
A''	-	-	08	358	tRasym(56)
A''	-	250	271	316	ω NN(52)
A''	-	180	114	122	NH2twist(69)

Abbreviations: v - stretching; b - in-plane bending; ω - out-of-plane bending; asymd - asymmetric; symd - symmetric; t - torsion; trig - trigonal; 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.^a

Table 3: The thermodynamical parameters of 1-aminopiperidine

Parameters	Method / Basis set	
	HF/ 6-311++G(d,p)	B3LYP/ 6-311++G(d,p)
Optimized global minimum energy, (Hartrees)	-302.25838723	-304.18530071
Total energy (thermal), E_{total} (k cal mol ⁻¹)	80.146	75.847
Heat capacity cv. (k cal mol ⁻¹)	22.871	24.375
Entropy.S (k cal mol ⁻¹ K ⁻¹)	77.951	79.295
Translational	0.889	0.889
Rotational	0.889	0.889
Vibrational	78.368	74.069
Zero point vibrational energy, (k cal mol ⁻¹)	319783.1	300858.7
Rotational constants (GHz)		
A	5.51699	5.51040
B	2.65457	2.61505
C	1.83454	1.80748
Dipole moment (Debye)		
μ_x	-0.6823	-1.1518
μ_y	1.3256	1.2042
μ_z	0.4694	0.2205
μ total	1.5630	1.6809

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