Vibrational spectroscopic (FT-IR, FT-Raman and NMR) and DFT analysis of 2-methoxy-3-(trifluoromethyl) pyridine

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ABSTRACT

In this study, the spectroscopic properties of 2-methoxy-3-(trifluoromethyl) pyridine (MTFMP) were investigated by FT-IR, FT-Raman, ^1H and ^{13}C NMR techniques. Fourier-transform Infrared (FT-IR) and Fourier-transform Raman (FT-Raman) spectra of MTFMP was recorded in the region $3500–400cm^{-1}$ and $3500–100cm^{-1}$, respectively. ^{13}C and ^1H NMR chemical shifts were calculated by using the gauge-independent atomic orbital (GIAO) method. The molecular structure and fundamental vibrational frequencies have been obtained from density functional theory (DFT) B3LYP and LSDA methods with 6-311++G(d,p) basis set calculations. Infrared intensities and Raman activities were calculated using DFT/ B3LYP method with 6-311++G(d,p) basis set. Molecular electrostatic potential (MEP) of the title compound was calculated to predict the static charges in the molecule. The thermodynamic properties at different temperatures were calculated, revealing the correlations between standard heat capacities, standard entropy and standard enthalpy changes with temperatures.

Keywords: DFT calculations, 2-methoxy-3-(trifluoromethyl) pyridine, vibrational analysis, MEP.
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INTRODUCTION

Pyridine is a prodigious heterocyclic aromatic compound serving as the parent compound of many biologically significant derivatives. Pyridine derivatives exhibited various types of biological activities like antimicrobial [1], antibacterial [2], antitumor [3] and anti-diabetic [4]. Several substituted pyridines are involved in many bio related activities which are used in pharmaceutical drugs as well as in the field of agriculture [5]. Pyridine heterocycles and its derivatives are a repeated moiety in many large molecules with interesting photo chemical, electrochemical and catalytic applications [6-8]. Vibrational spectra of substituted pyridine received considerable attention in the spectroscopic view of their obvious importance to biological systems and industrial significance [9-14].

To the best of our knowledge, neither the vibrational analysis nor the quantum chemical study of 2-methoxy-3-(trifluoromethyl) pyridine (MTFMP) has been reported. To fulfill the lacunae the current investigation of a systematic study on the optimized molecular structure, vibrational analysis based on FT-IR and FT-Raman spectral analysis, NMR chemical shift, MEP map and variation of thermodynamic properties with temperature of the title compound (MTFMP) have been carried out and reported.

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EXPERIMENTAL SECTION

The compound under investigation namely MTFMP was procured from Sigma–Aldrich chemicals, U.S.A with a stated purity of greater than 98%. The compound was used as such without further purification. The FT-IR spectrum of the compound was recorded in the region 3500-400cm^{-1} on a Perkin Elmer FT-IR Spectrophotometer. The FT-Raman spectrum of the title compound was recorded in the Bruker FRA 106/S instrument equipped with Nd:YAG laser source operating at 1064 nm line widths in the range of 3500–100cm^{-1}. The ^{1}H and ^{13}C NMR spectra was recorded on Bruker Avance III NMR spectrometer using DMSO as a solvent . Chemical shifts were reported in ppm relative to tetramethylsilane (TMS). The spectral measurements were carried out at Sophisticated Analytical Instrument Facility, IIT, Chennai, India.

Quantum chemical calculations

The gas phase geometry of the compound under investigation (MTFMP) in the ground state was optimized by using DFT/B3LYP(Becke3–Lee–Yang–Parr) and LSDA(Local Spin Density Approximation) level with the standard basis set 6-311++G(d,p) using Gaussian 09W [15] program package, invoking gradient geometry optimization [16]. The scaling factors have to be used to obtain considerably better agreement with experimental data. The computed harmonic frequencies at B3LYP/6-311++G(d,p) level of basis set were scaled by 0.981 for frequencies less than 1700cm^{-1} and 0.9615 for higher frequencies[17]. The scaled values used in DFT/LSDA/6-311++G(d,p) were 0.9937 for frequencies less than 1700cm^{-1} and 0.9865 for higher frequencies. ^{13}C and ^{1}H NMR were calculated in dimethylsulfoxide (DMSO) by using the gauge- independent atomic orbital (GIAO) method [18] with B3LYP /6-311++G(d,p) basis set level. To visualize variably charged regions of a molecule in terms of colour grading the Molecular Electrostatic Potential (MEP) map have been plotted. On the basis of theoretical frequencies obtained from density functional calculations at B3LYP and LSDA /6-311++G(d,p) level, the statistical standard thermodynamic parameters like entropy (S), Heat capacity (C) and enthalpy (H) were calculated.

RESULTS AND DISCUSSION

4.1 Molecular geometry

The optimized molecular structure along with the numbering of atoms of 2-methoxy-3-(trifluoromethyl) pyridine (MTFMP), obtained from GaussView program is shown in Fig.1. The molecule contains two substituent O-CH$_3$ and CF$_3$ in the pyridine ring. The global minimum energy obtained by the DFT/ B3LYP/6-311++G(d,p) for the optimized structure of the title compound is -700.0667 Hartrees.
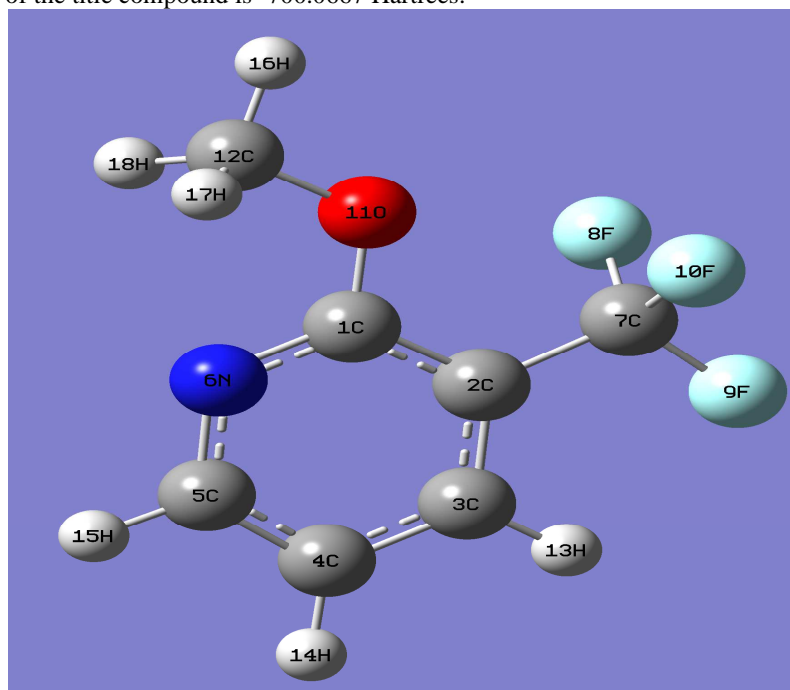

Fig.1 Optimized structure and atoms numbering of 2-methoxy-3-(trifluoromethyl) pyridine (MTFMP)

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4.2 Vibrational spectral analysis

The compound under investigation (MTFMP) belongs to C1 symmetry consists of 18 atoms having 48 modes of vibration active in IR and Raman spectra. The detailed vibrational assignments of fundamental modes of MTFMP along with observed and calculated frequencies are reported in Table 1. The calculated and experimental FT-IR, FT-Raman spectra are shown in Figs. 2 and 3, respectively. The correlation graph between observed and calculated frequencies of FT Raman and FT-IR is illustrated in Fig 4.
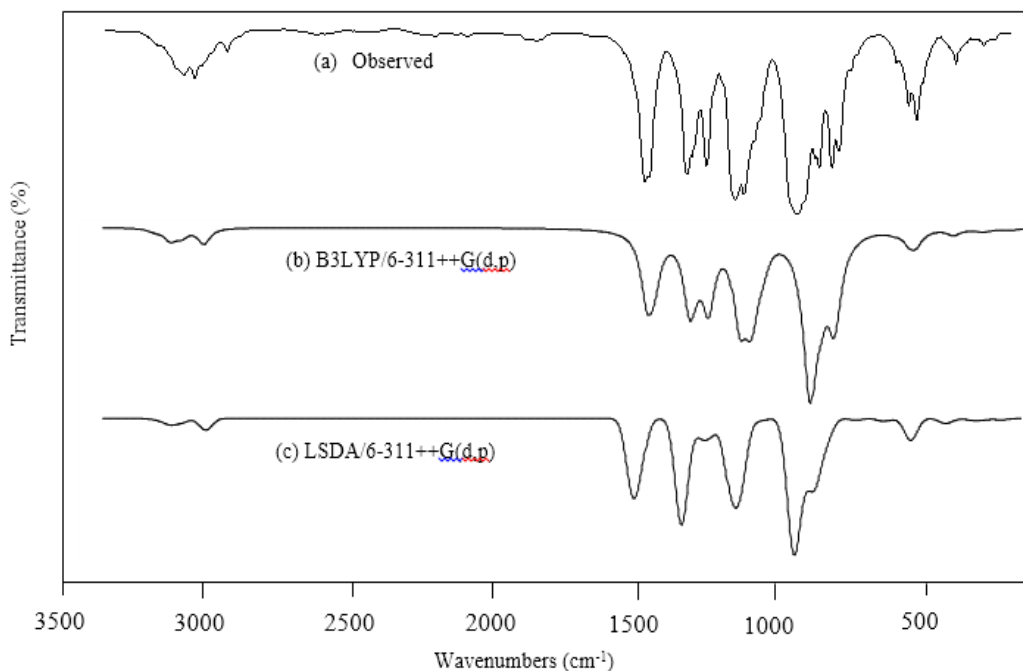

Fig. 2 Observed and calculated FT-IR spectra of 2-methoxy-3-(trifluoromethyl) pyridine (MTFMP)
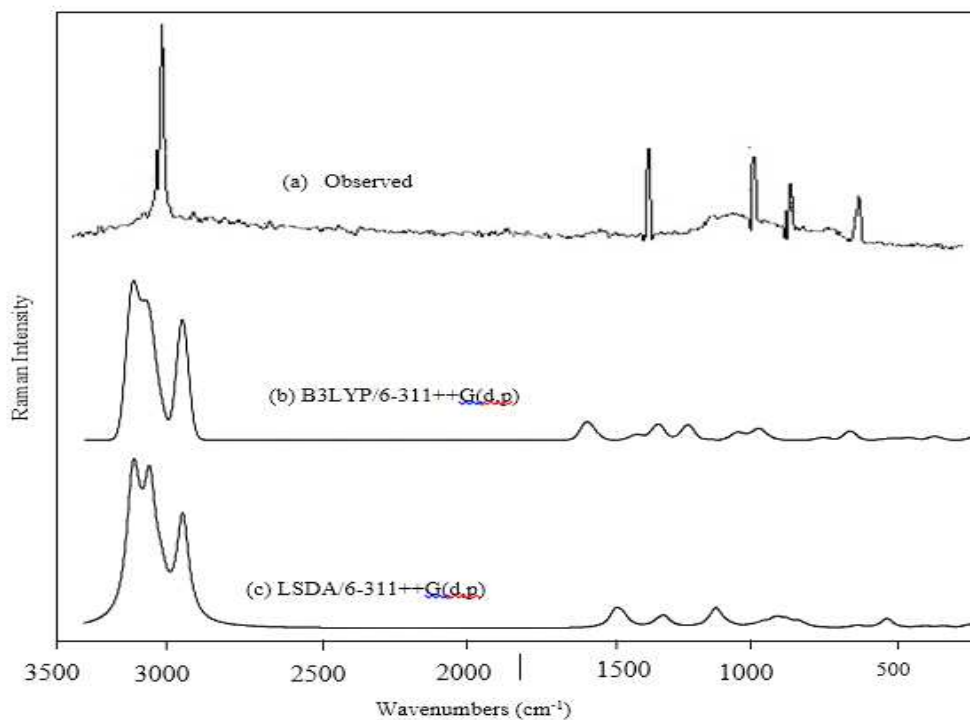

Fig. 3 Observed and calculated FT-Raman spectra of 2-methoxy-3-(trifluoromethyl) pyridine (MTFMP)

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C-C vibration

In the spectrum of pyridine and its derivatives, the ring stretching vibrations (C-C) are highly characteristic of the aromatic ring itself [19]. Normally the bands between 1400–1650cm^{-1} in pyridine derivatives are assigned to C- C stretching modes [20]. The theoretically computed C- C stretching vibrations by LSDA/6-311++G(d,p) at 1628,1603,1414 and 1387 and B3LYP/6-311++G(d,p) method at 1611, 1589, 1458 and 1419cm^{-1} shows good agreement with the experimental bands observed at 1601, 1590,1459 and 1417cm^{-1} in FT-IR and 1625,1584,1466cm^{-1} and 1416cm^{-1} in FT-Raman spectra as well as literature data. The breathing mode carbon is sensitive to the presence of substituents. In our present study the calculated values by LSDA and B3LYP methods at 1039, 1029cm^{-1} is assigned to C-C-C ring breathing mode. This mode is confirmed by the band observed at 1036 cm^{-1} in FT-IR and 1044 cm^{-1} in FT-Raman spectra. This assignment is also in line with the literature data [21]. The planar ring deformation modes for pyridine are usually observed at 605, 652 and 1030cm^{-1} [22]. The theoretically calculated value at 620,621 and 1026, 1013cm^{-1} by LSDA and B3LYP methods for the title compound for planar ring deformation is confirmed by the band observed at 610 and 1015cm^{-1} in the FT-IR and 612cm^{-1} and 1016cm^{-1} in FT-Raman. The frequency calculated at 762,773, 460,465 and 348,352cm^{-1} by LSDA and B3LYP methods assigned to the non-planar deformation is in good agreement with the experimental bands at 779 and 454cm^{-1} in FT-IR and 770, 454 and 367cm^{-1} in FT-Raman spectra.

C-H vibrations

The compound under investigation has three hydrogen atoms attached with the pyridine ring. The C-H stretching vibrations of this hetero aromatic structure are not much disturbed in the region 3000-3100cm^{-1} which is the characteristic region for C-H stretches [23]. The theoretically calculated frequencies by LSDA and B3LYP methods show that the three scaled C-H vibration are observed at 3057, 3026, 3082, 3064 and 3099, 3077cm^{-1}. The FT-IR bands observed at 3073cm^{-1} and the Raman bands observed at 3018,3068 and 3086 cm^{-1} have been assigned to C-H stretching vibrations. The C-H in-plane bending vibrations which occur in the region 1400 to 1200cm^{-1} are useful for characterization purpose [24]. The C-H in-plane bending vibrations computed in the region at 1233, 1250,1292,1280 and 1301, 1294cm^{-1} by LSDA and B3LYP methods show good agreement with FT-Raman spectral region at 1249, 1279 and 1296cm^{-1}. The C-H out-of plane bending vibrations are determined by the number of adjacent atoms on the ring and not very much affected by the nature of substitution [25], normally these vibrations occur in the region 1000-700cm^{-1}. In the present study, the FT-IR band observed at 779 cm^{-1} is assigned to C-H- out of plane bending vibration, the same is observed at 770cm^{-1} in FT-Raman spectra shows good agreement with the theoretically computed wavenumber at 762 and 773 cm^{-1} by LSDA and B3LYP methods.

O-CH$_3$ group vibrations

The molecule under investigation MTFMP has one methoxy group at the 2nd position. Generally the C-H stretching vibrations in methoxy group has been observed at lower wavenumber than the normal C-H stretching wavenumber for methyl group [26]. The expected asymmetric vibration of CH$_3$ in aromatic methoxy compounds are found in the region of 2985 ± 20cm^{-1} [27]. The calculated value at 3007, 2990cm^{-1} by LSDA and B3LYP methods is confirmed by the presence of a strong band at 2963cm^{-1} in FT-IR and 2965cm^{-1} in FT-Raman for this mode. The CH$_3$ symmetric stretching vibration at 2943cm^{-1} in FT-IR and 2939cm^{-1} in FT-Raman spectra is in good agreement with calculated values at 2933, 2920cm^{-1}. The methoxy group attached to an aromatic ring gives asymmetric stretching vibration of C-O-C in the range of 1310–1210cm^{-1} and symmetric stretching of C-O-C in the range of 1050–1010cm^{-1}[28]. In our present study the calculated value by LSDA and B3LYP methods at 1292, 1280 and 1026, 1013cm^{-1} as asymmetric and symmetric C-O-C stretching vibration. The presence of strong bands at 1271 and 1015cm^{-1} in FT-IR and 1279cm^{-1} and 1016cm^{-1} in FT-Raman spectrum was assigned to these modes. The O-CH$_3$ in plane bending mode has been calculated by LSDA and B3LYP methods at 566 and 564cm^{-1}. This is confirmed by the presence of a strong band at 577 and 579cm^{-1} FT-IR and FT-Raman spectra as well as the literature value [29]. CH3 torsional mode is identified at 158, 164 cm^{-1} by calculated values is confirmed by the presence of a Raman band at 169cm^{-1}. O-CH3 torsional mode is calculated by LSDA and B3LYP methods at 210 and 218cm^{-1} is confirmed by the presence of a peak at 221cm^{-1} in FT-Raman spectra.

C-N Vibrations

The C-N stretching vibration is always mixed with other bands and regularly assigned in the region 1382 - 1266cm^{-1} [30]. Accordingly, in our present study the calculated values at 1301, 1294cm^{-1} is supported by the presence of a band at 1296cm^{-1} in FT-Raman spectra is assigned to C-N stretching vibration. This is also supported by the literature [31]. The calculated values by LSDA and B3LYP methods at 760 and 745cm^{-1} is assigned to C-N in-plane bending vibration. This is supported experimentally by a band at 745cm^{-1} in FT-IR and 746cm^{-1} in FT-Raman

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spectra. The band observed at 454cm^{-1} in both FT-Raman and FT-IR spectrum is assigned to the C-N out-of-plane bending mode of the title compound which is in good agreement with the computed values at 460 and 465cm^{-1} by LSDA and B3LYP methods.

Table 1. Comparison of experimental (FT-IR and FT-Raman) wavenumbers(cm^{-1}) with the calculated harmonic frequencies of MTFMP using LSDA and B3LYP /6-311++G(d,p) basis set

S.No	FT-IR	FT-Raman	LSDA/ 6-311++ G(d,p)	B3LYP/ 6-311++ G(d,p)	B3LYP I_{IR}	B3LYP I_{Raman}	Vibrational Assignments
1			46	46	0.07	0.93	τ (CF$_3$)
2			98	97	2.50	1.35	γ (O-C)
3		119	115	111	5.10	2.27	ω (ring)
4		134	137	143	1.02	0.38	δ (C-O-C-C)
5		169	158	164	0.10	0.93	τ (CH$_3$)
6		221	210	218	0.37	0.64	τ (O-CH$_3$)
7		262	254	253	5.83	0.51	lattice vibration
8		334	328	327	2.32	3.42	β (CF$_3$)
9		352	348	344	3.30	3.31	γ (CF$_3$)
10		367	350	352	0.27	0.44	φ ring +γCF$_3$
11	454	454	460	465	1.24	0.51	φ ring +γC-N
12	478	479	482	481	3.29	5.66	ring sym. Def.
13	543	545	531	537	2.23	0.15	γ (CF$_3$)
14	577	579	566	564	6.78	3.25	β-(O-CH$_3$)
15	599	590	597	597	0.56	0.22	φ –ring
16	610	612	620	621	0.93	2.81	α (ring)+β(CF$_3$)
17	661	667	653	654	15.23	0.64	γ (C-C-N) +γ (C-H)
18	745	746	760	745	2.19	15.99	β (C-N)
19	779	770	762	773	33.68	0.22	γ(C-H) + φ –ring
20	804	791	780	794	27.02	0.05	ω (ring C-H)
21	841	847	846	841	4.66	3.96	β (C-C-C)
22	961	949	922	956	2.09	0.01	γ (C-H)
23	979	973	936	967	3.58	0.29	γ (C-H)
24	1015	1016	1026	1013	40.37	2.45	α-ring +υ_s (C-O-C)
25	1036	1044	1039	1029	188.33	7.17	(C-C-C) ring breathing
26	1074	1067	1065	1068	106.13	10.25	υ (C-H)
27	1086	1098	1095	1099	95.14	10.29	υ_s (C-F)
28		1113	1116	1103	289.01	2.35	υ_{as} (C-F)
29	1139	1126	1124	1136	26.02	4.76	δ-ring (C-H)
30		1144	1141	1150	0.05	2.67	γ (C-F) +ω (CH$_3$)
31		1175	1147	1180	4.26	2.13	ρ (CH$_3$)
32		1249	1233	1250	50.39	3.18	β (C-H)
33	1271	1279	1292	1280	107.85	4.51	β(C-H) + υ_{as}(C-O-C)
34	1303	1296	1301	1294	109.20	28.06	β (C-H) +υ (C-N)
35	1329	1326	1379	1323	192.58	1.59	ρ (C-H) + C-O
36	1417	1416	1387	1419	174.94	0.42	υ (C-C)
37		1455	1388	1456	9.52	11.72	τ (CH3)
38	1459	1466	1414	1458	29.31	4.38	υ (C-C)
39	1474		1456	1474	28.60	3.26	δ (CH$_3$)
40		1489	1476	1480	149.04	3.45	ω(CH$_3$)
41	1590	1584	1603	1589	94.36	13.64	υ(C-C)
42	1601	1625	1628	1611	157.19	25.68	υ(C-C)
43	2943	2939	2933	2920	40.43	170.18	υ_s(CH$_3$)
44	2963	2965	3007	2990	19.77	46.96	υ_{as} (CH$_3$)
45	2996	2976	3040	3023	17.51	82.61	υ_{as} (CH$_3$)
46		3018	3057	3026	12.51	115.29	υ (C-H)
47	3073	3068	3082	3064	3.55	81.30	υ (C-H)
48		3086	3099	3077	3.64	167.90	υ (C-H)

CF$_3$ Vibration
The title molecule MTFMP under consideration possess one CF$_3$ group. The bands observed at 1086cm^{-1} in FT-IR and 1098cm^{-1} in FT-Raman well correlated with the computed values by LSDA and B3LYP at 1095 and 1099cm^{-1} is assigned to symmetric C-F and the band at 1113cm^{-1} in FT-Raman well correlated with the computed value at 1116 and 1103cm^{-1} by LSDA and B3LYP methods is assigned to asymmetric C-F vibration. This is in good agreement with the literature data [32]. The C–F deformation vibrations usually occur in the regions 640–580cm^{-1}

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and 590–490cm^{-1} [33]. The experimental peaks at 543 and 610cm^{-1} in FT-IR and 545 and 612cm^{-1} in FT-Raman spectra of the title compound confirm the presence of out of plane and in-plane bending vibrations of CF$_3$. The calculated values by LSDA and B3LYP methods at 531,537 and 620, 621cm^{-1} is well correlated with experimental as well as the literature data. CF$_3$ rocking mode usually appears in the ranges of 450–350cm^{-1} and 350–260cm^{-1} [34]. The computed value at 328, 327 and 348, 344cm^{-1} by LSDA and B3LYP methods is assigned to CF$_3$ in-plane and CF$_3$ out of plane rocking. This is supported by the presence of bands at 334 and 352cm^{-1} in FT-Raman spectra. In the calculated frequency of both the methods the CF$_3$ torsional mode occurs at 46 cm^{-1}. It is difficult to observe the torsional motion in the FT-IR and FT-Raman spectra. This is because of the low wave number.
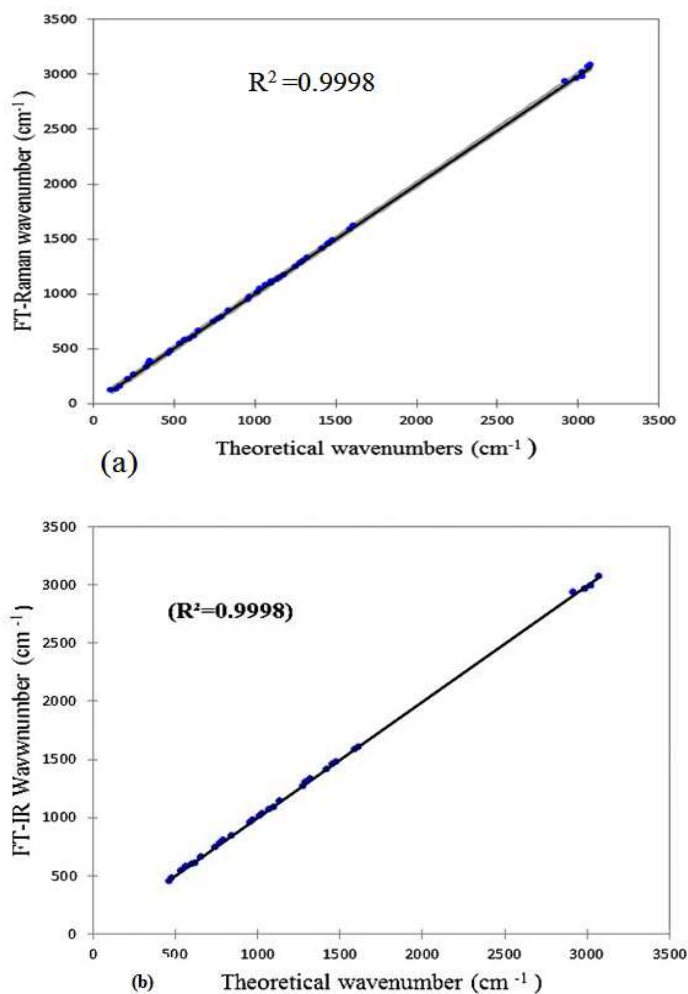

Fig 4. Correlation graph between observed and calculated B3LYP/6-311++G(d,p) frequencies of (a) FT-Raman and (b) FT-IR

4.3 NMR Calculations

Nuclear magnetic resonance (NMR) is a research technique that is used in many disciplines of scientific research, medicine, various industries and also determination of biological macro molecules. Due to their higher sensitivity, they are valuable for structural investigations. The combined use of NMR and computer simulation methods offers a powerful way to interpret and predict the structure of large biomolecules [35]. For reliable calculations of magnetic properties, accurate predictions of molecular geometries are essential. Firstly, full geometry optimization of MTFMP was performed at the gradient corrected density functional level of theory using the hybrid B3LYPand LSDA method. Then gauge- independent atomic orbital (GIAO) ^{1}H and ^{13}C chemical shift calculations of the compound was done by same methods using 6-311++G(d,p) basis set IEFPCM/DMSO solution [36]. Relative chemical shifts were estimated by using the corresponding TMS shielding calculated in advance at the same

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theoretical level as the reference. The isotropic shielding values were used to calculate the isotropic chemical shifts with respect to the TMS. The value of σ^{TMS} is 182.46 and 31.88 ppm for ^{13}C and ^{1}H respectively.

Usually the range of ^{13}C NMR chemical shifts for a typical organic molecules occur larger than 100 ppm [37]. In our present study, there are seven carbon signals calculated theoretically and tabulated in table 2, of which five carbon were located in aromatic region. Among the seven carbons, the carbon atom located at atom number 12 is in the upfield chemical shift region. The five aromatic carbons which give signals in overlapped areas of the spectrum with chemical shift values from 100 to 150 ppm. The chemical shift value of carbon C1 is greater than other carbons due to the presence of the resonating effect of lone pair in the oxygen and the adjacent electronegative Nitrogen. The chemical shift value of C5 is the next higher due to the influence of electronegative nature of Nitrogen atom. The C12 atom has the smallest shift in all chemical shift localized on the methoxy group. The observed and calculated chemical shift values show correlation with each other.

The proton chemical shift (^{1}H NMR) of organic molecules generally varies greatly with the electronic environment of the proton. Usually, Hydrogen attached to or nearby electron- withdrawing atom or group can decrease the shielding and move the resonance of attached proton towards a higher frequency, whereas electron-donating atom or group increases the shielding and moves the resonance towards a lower frequency [38]. In our present investigation, the molecule under study contains six hydrogen atoms. All the six atoms show the chemical shift in both experimental and theoretical methods. Among the six atoms 3 hydrogen atoms are in the methoxy group and the remaining three are located in the aromatic ring. The H16, H17 and H18 attached to the electron donating methoxy group shows an upfield shift. The chemical shift of proton numbered H15 is highly towards the downfield when compare with other protons due to the influence of electronegative adjacent Nitrogen atom. The observed chemical shift value is good in agreement with calculated values.

The correlation graph between the experimental and calculated ^{13}C NMR and ^{1}H NMR chemical shifts of title molecule are represented in Fig. 5. The experimental ^{13}C and ^{1}H NMR spectra of the title compound is presented in Fig.6 and fig.7. The relations between the calculated B3LYP/6-311++G(d,p) and experimental chemical shifts are usually linear and described by the following equation:

$\delta_{cal}= 1.04055\delta_{exp} -2.63365$ for ^{13}C ($R^2=0.9922$)
$\delta_{cal}= 1.02651\delta_{exp} -0.18685$ for ^{1}H ($R^2=0.9988$)

Table 2. Experimental and theoretical B3LYP and LSDA ^{13}C and ^{1}H isotropic chemical shift of MTFMP (with respect to TMS) in DMSO (all values in ppm)

Atom	Experimental	Calculated		Atom	Experimental	Calculated	
		B3LYP	LSDA			B3LYP	LSDA
1C	160.87	166.98	163.92	13H	7.85	8.32	8.86
2C	119.75	117.58	118.02	14H	6.94	7.37	7.96
3C	136.27	143.02	142.09	15H	8.32	8.68	9.25
4C	116.02	120.39	122.80	16H	3.92	4.01	4.89
5C	150.42	157.78	158.23	17H	4.14	4.03	4.83
7C	136.16	133.82	136.92	18H	4.04	4.02	4.83
12C	53.89	55.06	55.17				

4.4 The Molecular Electrostatic Potential

The Molecular Electrostatic Potential (MEP) which is related to total charge distribution of the molecule provides the correlations between the molecular properties such as dipole moments, partial charges, chemical reactivity and electronegativity of molecules [39,40]. The MEP map of the title compound was calculated by B3LYP/6-311++G(d,p) method to predict the static charges in the molecule. The study of MEP leads to the better understanding of complex biological processes involving the charge-dipole, dipole-dipole, and quadrupole -dipole interactions as well as displays molecular size, shape and electrostatic potential value.
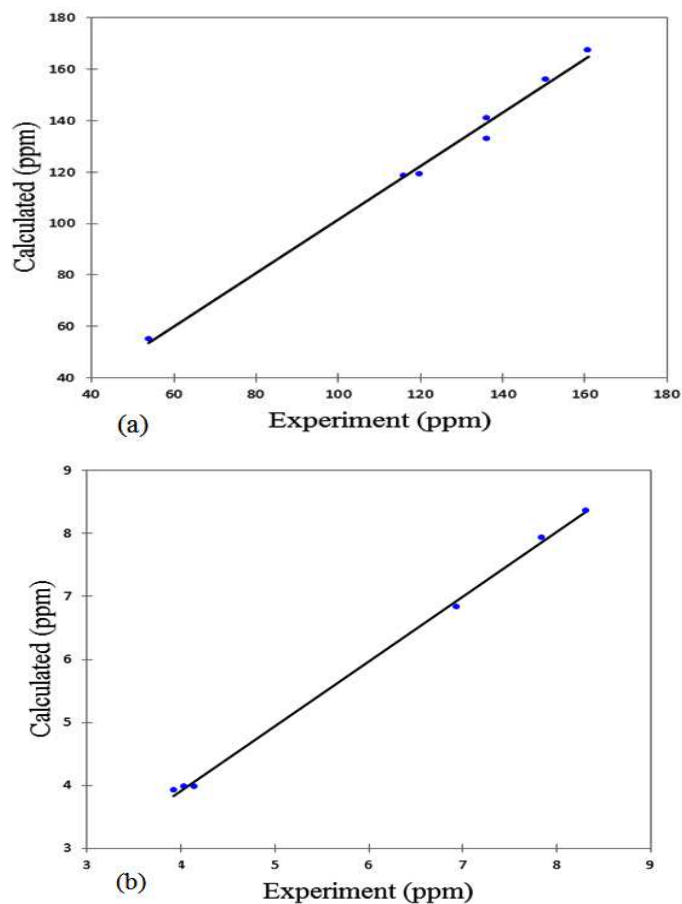
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Fig. 5 Correlation graph between calculated (B3LYP/6-311++G(d,p)) and experimental chemical shifts (a) ^{13}C and (b) ^{1}H NMR of MTFMP

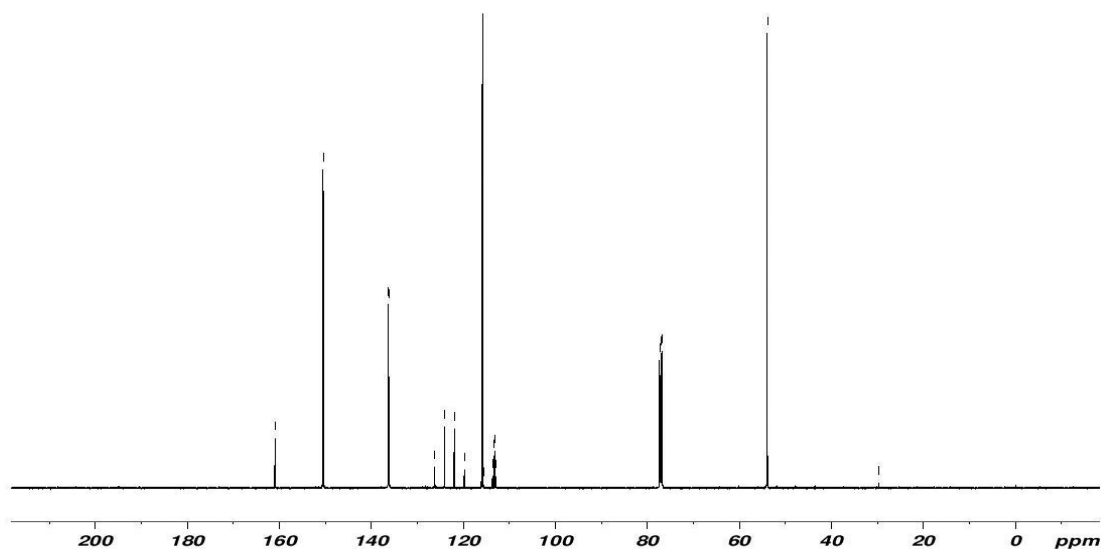**Fig. 6 Experimental ^{13}C NMR spectra of 2-methoxy-3-(trifluoromethyl) pyridine (MTFMP)**
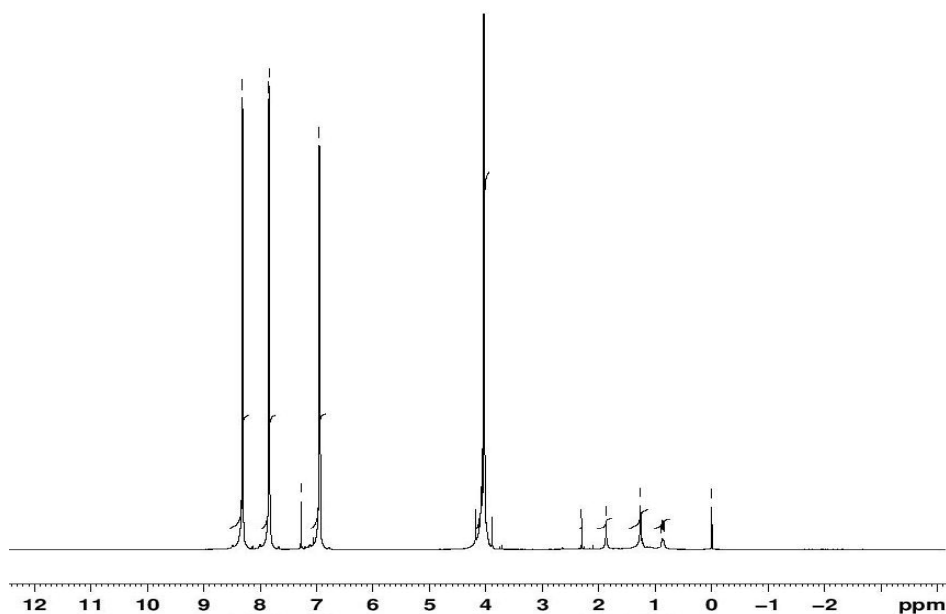
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Fig. 7 Experimental ^{1}H NMR spectra of 2-methoxy-3-(trifluoromethyl) pyridine (MTFMP)

MEP surface diagram shown in Fig.8 is used to visualize variably charged regions of a molecule in terms of colour grading. Areas of red (negative MEP) are characterized by an abundance of electrons or greatest electron density. Areas of blue (positive MEP), are characterized by a relative absence of electrons. The electrostatic potential increases in the order red < orange < yellow < green < blue. The colour code of the maps in the range -3.318 a.u.(deepest red) to 3.318 a.u.(deepest blue) in the title molecule, where the blue colour indicates the strongest attraction and the red colour indicates the strongest repulsion. As can be seen from the MEP map of the title compound the maximum negative regions V(r) are associated with the lone pair oxygen(O_{11}) atom having value of -0.33013 a.u. The maximum positive regions localized on the H_{14} atom in the ring have the value of +0.02781 a.u. However, the H atoms at the O-CH_3 group have smaller values than the H atoms in the ring. From this result, we infer that the oxygen atom indicate the strongest repulsion and H atoms indicate the strongest attraction.
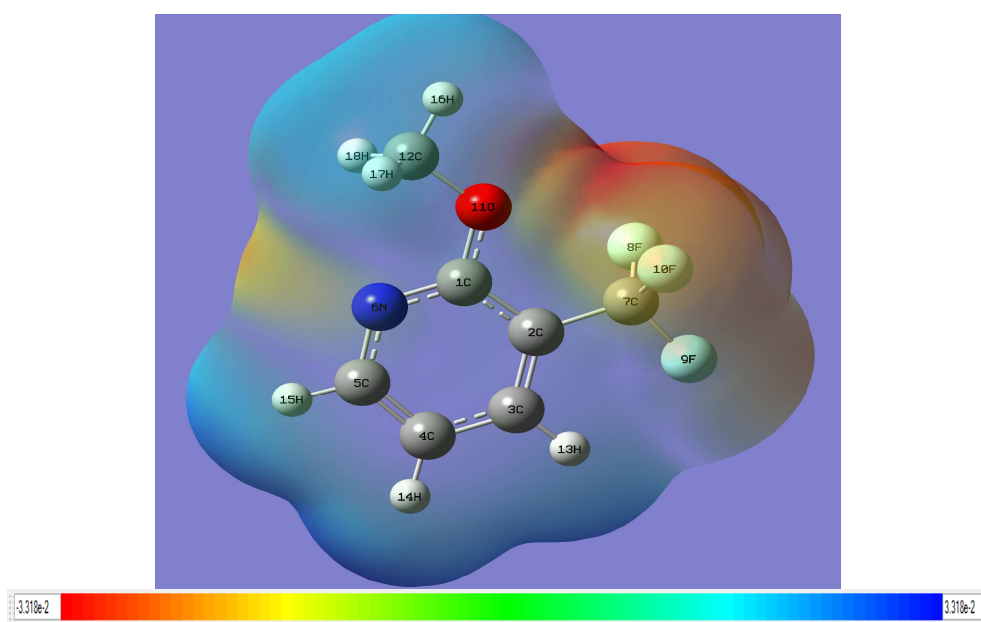

Fig. 8 Molecular electrostatic potential map of 2-methoxy-3-(trifluoromethyl) pyridine(MTFMP)

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4.5 Thermodynamic properties

On the basis of theoretical frequencies obtained from density functional calculations at B3LYP/6-311++G(d,p) level, the statistical standard thermodynamic parameters like entropy (S), Heat capacity (C) and enthalpy (H) were calculated using perl script THERMO. PL [41] and listed in table 3. It can be observed that these thermodynamic functions are increasing with temperature ranging from 100 to 1200 K due to the fact that the molecular vibrational intensities increase with temperature [42]. While performing the calculation, the molecule was considered to be at room temperature of 298.15 K and one atmospheric pressure. The correlation equations between heat capacity, entropy, enthalpy changes and temperatures were fitted by quadratic formulas, and the corresponding fitting factors (R^2) for these thermodynamic properties are 0.9996 , 0.9999 and 0.9995 respectively. The corresponding fitting equations are as follows and the correlation graph of those shown in Fig 9.

$C = 22.1545 + 0.5693T - 2.5 \times 10^{-4} \ T^2$ ($R^2 = 0.9996$)
$S = 234.5405 + 0.6853T - 1.8 \times 10^{-4} \ T^2$ ($R^2 = 0.9999$)
$H = -7.2267 + 0.0856T + 1.5 \times 10^{-4} \ T^2$ ($R^2 = 0.9995$)

Table 3. Thermodynamic properties of MTFMP at different temperatures at B3LYP/ 6-311++G(d,p) level.

T (K)	C (J/ mol.K)	S (J/ mol.K)	ΔH (kJ/mol)
100	78.58	297.93	5.36
200	123.86	366.35	15.49
298.15	168.36	424.11	29.83
300	169.19	425.16	30.14
400	211.47	479.75	49.22
500	247.05	530.9	72.21
600	275.6	578.56	98.4
700	298.37	622.82	127.14
800	316.74	663.9	157.92
900	331.78	702.11	190.37
1000	344.25	737.73	224.19

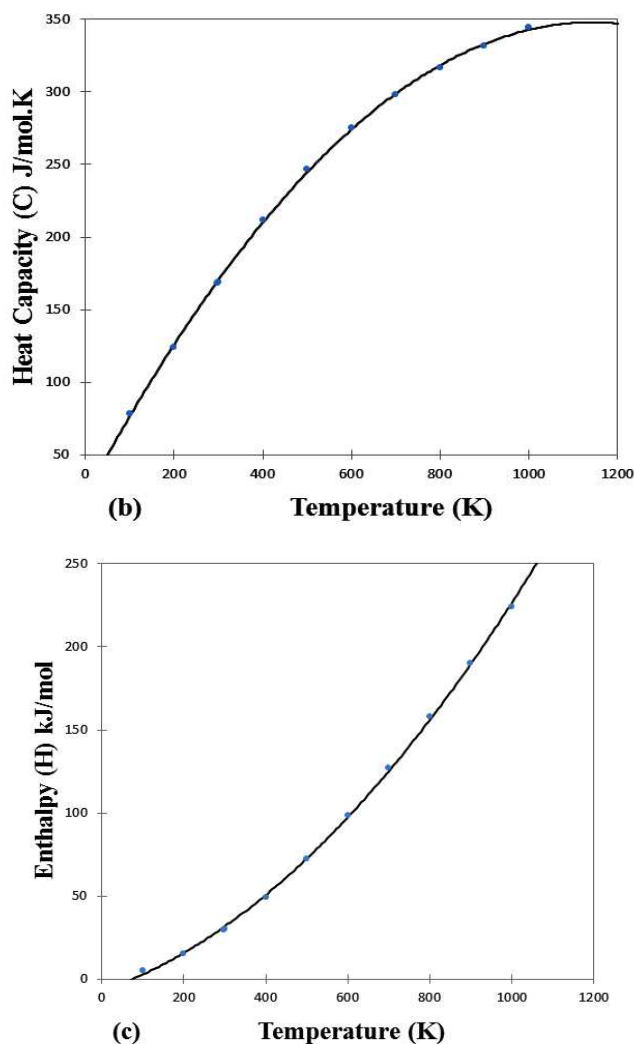(a)   **Temperature (K)**

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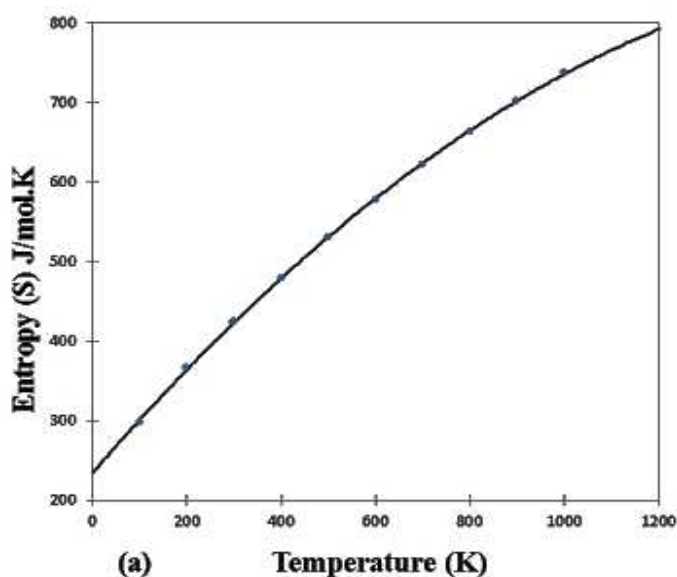
Fig. 9 Correlation graph between temperature and (a) entropy (b) Heat capacity (c) enthalpy of MTFMP

CONCLUSION

In the present work, a complete vibrational analysis and electronic properties of MTFMP was performed at DFT methods B3LYP and LSDA at 6-311++G(d,p) basis set level. The computed vibrational wavenumbers were assigned and compared with experimental FT-IR and FT-Raman spectra. The observed and stimulated spectra are in good agreement and show a good frequency fit of the title molecule. The chemical shift of ^{13}C and ^{1}H of the title compound calculated in DMSO on comparison with the experimental was found to have a linear relation. The MEP map shows the negative potential sites are around the electronegative oxygen atom and the positive potential are around the hydrogen atoms. The correlations between the statistical thermodynamics and temperature were also obtained. It was ascertained that the heat capacity, entropy and enthalpy increase with the increasing temperature owing to the increase in the intensities of the molecular vibrations with increasing temperature.

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