



# Scaled quantum mechanical study of 2-Thiophene Carbohydrazide

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## Abstract :

The FTIR and FT-Raman spectra of 2- Thiophene Carbohydrazide (2TCH) have been measured in the range 4000-400  $\text{cm}^{-1}$  and 3500-50  $\text{cm}^{-1}$ , respectively. Utilising the observed FTIR and FT-Raman data, complete vibrational assignment and analysis of the fundamental modes of the compound have been carried out by employing the B3LYP/6-311+G(d,p) method for optimized geometries. The Total Energy Distribution (TED) values obtained reflect the correctness of the vibrational assignments. The thermodynamic properties, Mulliken charges, APT charges and Natural Bond Orbitals(NBO) are also analysed.

**Keywords:** FTIR, FT-Raman spectra, 2- Thiophene Carbohydrazide (2TCH), Density functional theory, Total energy distribution, NBO

## 1 INTRODUCTION :

Hydrazides and hydrazones, the acylated derivatives [1] of hydrazine besides being useful for a number of biological properties, hydrazides are important starting material for a wide range of derivatives utilizable in pharmaceutical products and as surfactants. The hydrazones derivatives are used as fungicides, and in the treatment of diseases such as tuberculosis, leprosy and mental disorders. Biological assessment of fatty hydrazide and the derivatives have been the focus of earlier investigative studies [2,3]. Hydrazides have recently become attractive to theoreticians as well as experimentalists due to the biological significance particularly in medicinal and enzyme chemistry. Many substituted hydrazides are employed in the treatment of psychotic and psychoneurotic conditions. Carboxylic acid hydrazides are known to exhibit strong antibacterial activities which are enhanced by complexation with metal ions. The vibrational spectral studies of hydrazone are analysed by Durig et. al., [4,5]. The literature survey reveals that no theoretical calculations or detailed vibrational infrared and Raman analysis have been performed on 2-Thiophene Carbohydrazide (2TCH) molecule so far. So, in the present investigation, the geometrical parameters and vibrational wave numbers of 2TCH are investigated by using ab initio HF and B3LYP calculations with 6-31+G(d,p) basis set.

Specific scale factors are also used and employed in the predicted frequencies. The thermodynamic properties, Mulliken charges, APT charges and Natural Bond Orbitals(NBO) are also analysed.

## 2 EXPERIMENTAL DETAILS

The pure compound 2TCH was purchased from Lancaster chemical company, U.K. and used as such without any further purification. The room temperature Fourier transform infrared (FT-IR) spectrum of 2TCH is recorded in the range of 4000 - 400  $\text{cm}^{-1}$  at a resolution of  $\pm 1 \text{ cm}^{-1}$  using a BRUKER IFS 66V FT-IR spectrophotometer equipped with a cooled MCT detector. Boxcar apodization is used for the 250 averaged interferograms collected for both the samples and background. The FT-Raman spectrum is recorded on a computer interfaced BRUKER IFS-66V model interferometer, equipped with FRA 106 FT-Raman accessories in the 3500–50  $\text{cm}^{-1}$  Stokes region, using the 1064 nm line of Nd:YAG laser for excitation operating at 200 mW power. The reported wave numbers are believed to be accurate within  $\pm 1 \text{ cm}^{-1}$

## 3 COMPUTATIONAL DETAILS

Hartree-Fock (HF) and density functional theory (DFT) calculations are carried out for 2TCH using GAUSSIAN 09W program package [6]. The geometry optimization was carried out using the 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 [7] using the correlation function of Lee et al., [8], implemented with the same basis set for better description of the bonding properties of amino 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 multiple scaling of the force constants are performed according to SQM procedure [9] using selective scaling in the natural internal coordinate representation [10]. 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 [11,12]. The systematic comparison of the results from DFT theory with results of experiments has shown that the method using B3LYP functional is the most promising in providing correct vibrational wave numbers. The calculated geometrical parameters are compared with X-ray diffraction result [13,14].

## 4 RESULTS AND DISCUSSION

### 4.1. Molecular geometry

The optimized molecular structure of 2TCH along with numbering of atoms is shown in Fig. 1. The optimized parameters of 2TCH obtained by HF/6-31+G(d,p) and DFT-B3LYP/6-31+G(d,p) levels are listed in Table 1. From Table 1, most of the optimized bond lengths and bond angles slightly deviate from the experimental ones, because the molecular states are different during experimental and theoretical processes. One isolated molecule is considered in gas phase in theoretical calculation, whereas many packed molecules are treated in condensed phase during the experimental measurement. The thiophene ring is planar, and also O and C atoms of carbonyl groups are lying approximately in the plane as evident from the torsional angle  $\text{C9-C4-S5-C1} = 180.0^\circ$  by B3LYP/6-31+G(d,p), respectively. These values are comparable with reported value

available in the literature [15]. In ring, the C–C bond lengths vary from 1.0674Å to 1.7787Å and the bond angles C1–S2–C3 and S2–C3–C4, which are calculated as 112.986° and 123.767°, respectively by the B3LYP/6-31+G(d,p) method. These values of ring angles are also evident for the five membered ring. The calculated geometric parameters also represent good approximations and they can be used as foundation to calculate the other parameters for the compound.

#### 4.2. Vibrational Frequencies

**Analysis** The molecular structure of 2TCH belongs to C<sub>1</sub> point group symmetry. For C<sub>1</sub> symmetry there would not be any relevant distribution. The molecule consists of 15 atoms and expected to have 39 normal modes of vibrations of the same A species under C<sub>1</sub> symmetry. The experimental IR, Raman frequencies along with theoretically calculated both unscaled and scaled frequencies are presented in Table 2. The FT-IR and FT-Raman spectra of the 2TCH are shown in Figs. 2 and 3, respectively.

##### C-H Vibrations

Aromatic compounds commonly exhibit multiple weak bands in the region 3200–3300 cm<sup>-1</sup> due to aromatic C–H stretching vibration [16]. In this region, the bands are not affected appreciably by the nature of substituents. The C–H stretching mode usually appears with strong Raman intensity and is highly polarized. May be owing this high polarization, Raman bands have not been observed in experimental spectrum. In the FT-IR spectrum of 2TCH, the bands at 3284, 3259 and 3237 cm<sup>-1</sup> are assigned to C–H stretching vibrations of hetrocyclic group. The theoretically computed wavenumber by B3LYP method falls in the range at 3244–3290 cm<sup>-1</sup> and is assigned to C–H stretching vibration as shown in Table 2. The TED corresponding to this vibration contributing greater than 80%. The C–H in-plane bending frequencies appear in the range 1000–1300 cm<sup>-1</sup> and are very useful for characterization purpose [17]. For 2TCH, the C–H in-plane bending vibrations appeared in FTIR spectrum at 1232, 1117 and 1089 cm<sup>-1</sup> show good agreement with computed wavenumber by B3LYP/6-31+G(d,p) method at 1239, 1126 and 1081 cm<sup>-1</sup>. The C–H out-of-plane bending vibrations are strongly coupled vibrations and occur in the region 1000–750 cm<sup>-1</sup> [18]. The aromatic C–H out-of-plane bending vibrations of 2TCH are observed at 926, 874 and 749 cm<sup>-1</sup> in FT-IR are well correlated with B3LYP/6-31+G(d,p) method at 919, 867 and 757 cm<sup>-1</sup>.

##### C=O Vibrations

The structural unit of C=O has an excellent group frequency, which is described as a stretching vibration. Since the C=O group is a terminal group, only the carbon is involved in a second chemical bond. This reduces the number of force constants determining the spectral position of the vibration. Almost all carbonyl compounds have a very intense and narrow peak in the range of 1800–1600 cm<sup>-1</sup> [19,20] or in other words the carbonyl stretching frequency has been most extensively studied by infrared spectroscopy [21]. The multiple bonded group is highly polar and therefore gives rise to an intense infrared absorption band in the region 1700–1800 cm<sup>-1</sup>. The carbon–oxygen double bond is formed by  $\sigma$  bonding between carbon and oxygen. Because of the different electro negativities of the carbon and oxygen atoms, the bonding electrons are not equally distributed between the two atoms. The following two resonance forms contribute to the bonding of the carbonyl group  $\text{>C=O} \leftrightarrow \text{>C}^+ \text{O}^-$ . The lone pair of electrons on oxygen also determines nature of the carbonyl group [22]. The C<sub>9</sub>=O<sub>10</sub> stretching vibration is observed at 1686 cm<sup>-1</sup> in FT-IR spectrum coincides with the literature [20]. The in-plane and out-of-plane bending vibrations are observed at 667 and 451 cm<sup>-1</sup> in FTIR spectrum, respectively.

##### N–H Vibrations

The hetero aromatic molecule containing an N–H group shows its stretching absorption in the region 3500–3220 cm<sup>-1</sup>. This is usual range of appearance for NH<sub>2</sub> vibrations. The position of absorption in this region depends upon the degree of hydrogen bonding, and hence upon the physical state of the sample or the polarity of the solvent [23]. The vibrational bands due to the N–H stretching are sharper and weaker than those of

C–O stretching vibrations by virtue of which they can be easily identified [24]. The N–H stretching fundamental of piperidine is observed in the vapour phase at  $3364\text{ cm}^{-1}$ . Gulluoglu et. al., [25,26] observes in the liquid phase at  $3340\text{ cm}^{-1}$  for the N–H stretching of piperidine. In the present investigation, the FT-IR band observed at  $3323\text{ cm}^{-1}$  is assigned for N–H stretching vibration. The TED also confirms that this vibration is a pure mode of contributing greater than 90%. The in-plane and out-of-plane bending vibrations of N–H group are observed at  $1229$  and  $696\text{ cm}^{-1}$  in FT-Raman spectrum and also supported by the literature [27]. NH<sub>2</sub> Vibrations The 2TCH molecule under consideration posses NH<sub>2</sub> 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 are generally observed in the region  $3500\text{--}3300\text{ cm}^{-1}$  for NH stretching,  $1700\text{--}1600\text{ cm}^{-1}$  for scissoring and  $1150\text{--}900\text{ cm}^{-1}$  for rocking deformation. In the present investigation, the asymmetric and symmetric modes of NH<sub>2</sub> group are assigned at  $3412$  and  $3352\text{ cm}^{-1}$  in FT-IR spectrum, respectively. The band observed at  $1630\text{ cm}^{-1}$  in FT-IR spectrum is assigned to NH<sub>2</sub> scissoring mode. The rocking, wagging and twisting deformation vibrations of NH<sub>2</sub> contribute to several normal modes in the low frequency region. The band observed at  $1612\text{ cm}^{-1}$  in FT-IR is assigned to NH<sub>2</sub> rocking vibration and the bands observed at  $483$  and  $597\text{ cm}^{-1}$  in FT-Raman are assigned to NH<sub>2</sub> wagging and twisting modes coincide with the literature [28].

#### C–N Vibrations

The C–N stretching frequencies in the side chain are a rather difficult task since there are problems in identifying these frequencies from other vibrations. The C–N stretching usually lies in the region  $1400\text{--}1200\text{ cm}^{-1}$ . Since, mixing of bands is possible in this region. However, with the help of force field calculations the C–N vibrations are identified [29]. In this study, the C–N stretching vibrations of 2TCH are found at  $1365\text{ cm}^{-1}$  in the FT-Raman spectrum. The C–N bending vibrations and deformations of 2TCH are summarized in Table 2.

### 5 THERMODYNAMIC PROPERTIES

The thermodynamic parameters such as total thermal energy, heat capacity at constant volume, entropy, vibrational energy, zero point vibrational energy and rotational constants are calculated employing HF/6-31+G(d,p) and B3LYP/6-31+G(d,p) methods and they are presented in Table 3. Dipole moment reflects the molecular charge distribution and is given as a vector in three dimensions. Therefore, it can be used as descriptor to depict the charge movement across the molecule. Direction of the dipole moment vector in a molecule depends on the centers of positive and negative charges. Dipole moments are strictly determined for neutral molecules. For charged systems, its value depends on the choice of origin and molecular orientation.

### 6 MULLIKEN'S ATOMIC CHARGE

The bonding capability of a molecule depends on the electronic charge on the chelating atoms. The atomic charge values are obtained by the Mulliken population analysis [30]. To validate the reliability of the results, the Mulliken population analysis of 2TCH is calculated using HF and B3LYP levels of theory with 6-31+G(d,p) basis set. The corresponding characteristics of the atomic charge populations of the constituent atoms and bonds are presented in Table 4. In 2TCH molecule the charge on C1, C2 and C3 atoms are negative whereas the remaining carbons, sulphur and hydrogen atoms are positively charged. The result suggests that the atoms bonded to the hydrogen atom and the oxygen atoms are electron acceptor. The negative values on C1, C2 and C3 atom in the aromatic ring lead to a redistribution of electron density [31]. Due to these strong negative charges, C4 and C9 atoms accommodate higher positive charge and become more acidic.

### 7 APT CHARGES

The Atomic Polar Tensor charges for the 2TCH calculated at the HF/6-31+G(d,p) and B3LYP/6-31+G(d,p) levels are collected in Table 5. In the present study, the hydrogen atoms attached to the sites C1, C2 and C3

may pull nearly equal amount of charges from the respective carbon atoms and hence, induce nearly equal amount of charges on them. But it is found that the atomic charges on the site C1, C2 and C3 are less than that at the site C4. This is because C4 is attached with carbohydrazone group whereas C1, C2 and C3 are attached with a hydrogen. Among all the carbon atoms C9 is the only electro positive and all the remaining carbon atoms are electro negative. As the oxygen atom is the most electronegative among all the atoms, it possesses the highest atomic charge [32]. Next to that nitrogen atoms gain more electronegative since they pull more charges. Sulfur possesses the smallest electro positive value.

## 8 NBO ANALYSIS

It has become well known that among theoretical methods, natural bond orbital (NBO) analysis developed by Weinhold et. al., [33-35] is an extraordinary useful formalism to evaluate delocalization effects. In this theory the electron delocalization is signified as the interaction between occupied molecular natural orbitals in one fragment of the molecule with particular unoccupied molecular orbitals in another fragment of the molecule. According to this theory the total electron density is characterized by localized orbitals, which allows the representation of molecules in terms of localized Lewis-type structures. The electron delocalizations, which can be considered as an intramolecular donor-acceptor interaction of localized bonds or lone pairs with antibonding orbitals, result in the departure from the 65 hypothetical idealized Lewis structures due to conjugation. Amidst such conjugative interactions the electron density is transferred from occupied orbitals to unoccupied orbitals resulting in a loss of occupancies of the localized bonds and lone pairs, and in larger occupancies of the antibonding orbitals. Second-order perturbation energies (referred to as  $E(2)$ ) that are calculated by the NBO scheme reflect the strength of donor-acceptor (or bond-antibond) hyperconjugative interactions between NBOs and estimate the energetic importance of these interactions [36]. The natural bond orbital (NBO) analysis provides a description of the structure of a conformer by a set of localized bond, antibonds and Rydberg extravalence orbitals. Stabilizing interactions between filled and unoccupied orbitals and destabilizing interactions between filled orbitals can also be obtained from this analysis [34,37-39]. Therefore, NBO theory is a valuable complement to the energetic and structural data presented above. DFT level computation is used to investigate the various second order interaction between the filled orbitals of one subsystem and vacant orbitals of another subsystem, which is a measure of the delocalization or hyperconjugation [40].

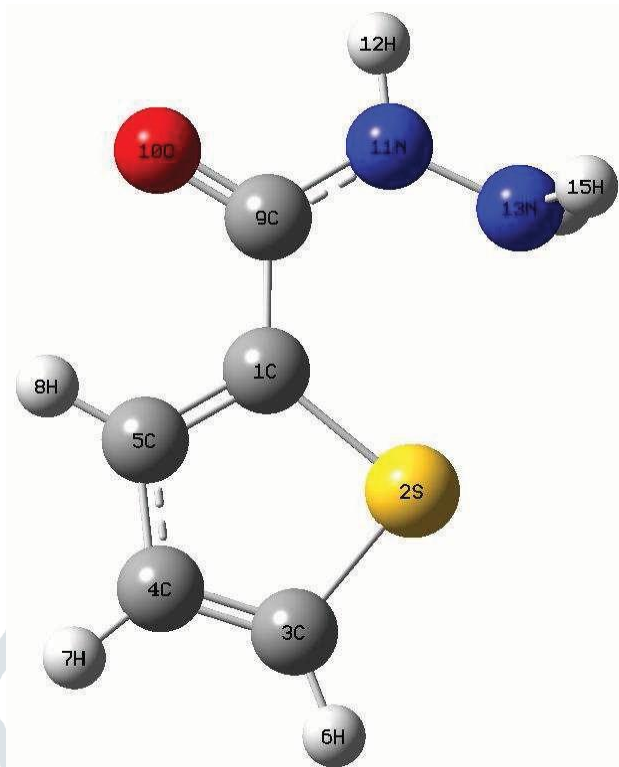
## 9 CONCLUSION

DFT and ab initio calculations have been carried out on the structure and vibrational spectra of 2-Thiophene Carbohydrazone. Comparison between the calculated and experimental structural parameters indicates that B3LYP results are in good agreement with experimental values. Vibrational frequencies calculated by B3LYP/6-31+G(d,p) method agree well with experimental results. The assignments made at higher level of theory with higher basis set with only reasonable deviations from the experimental values, seem to be correct. The various properties of 2TCH are discussed by studying non-linear optical effects, Thermodynamic properties, Mulliken atomic charges and APT charges. The NBO analysis of the molecule shows strong intramolecular hyperconjugative interactions.

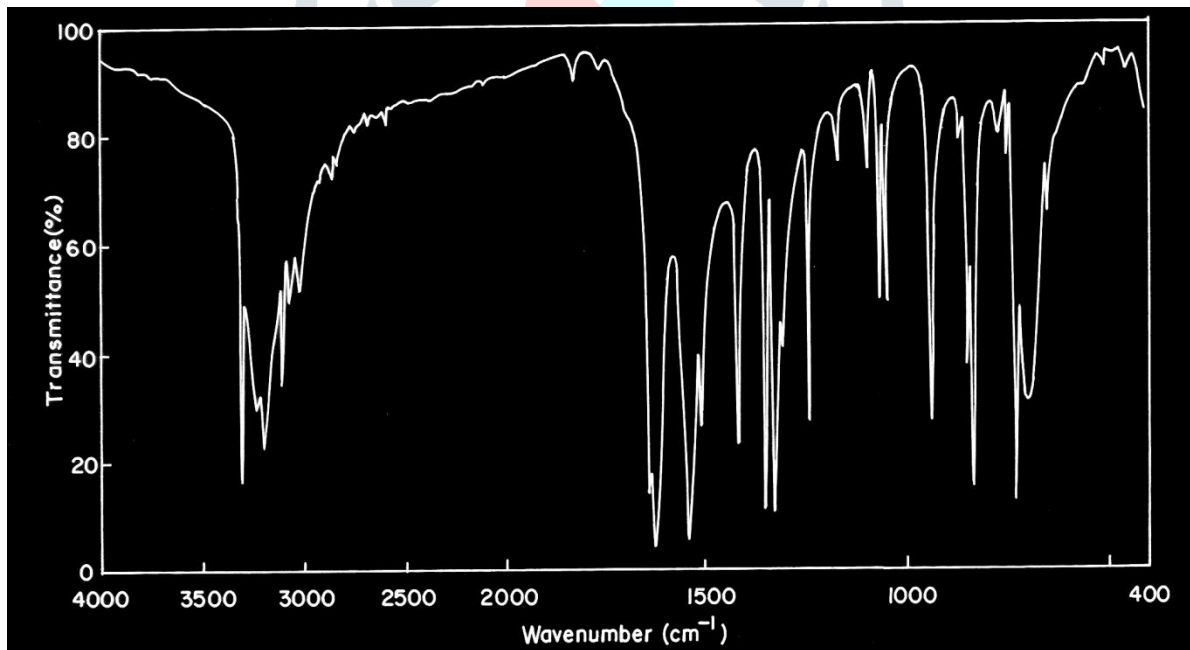
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**Fig.1: Molecular structure of 2-thiophene carbohydrazide**



**Fig. 2: The FT-IR spectrum of 2-thiophene arbohydrazide**

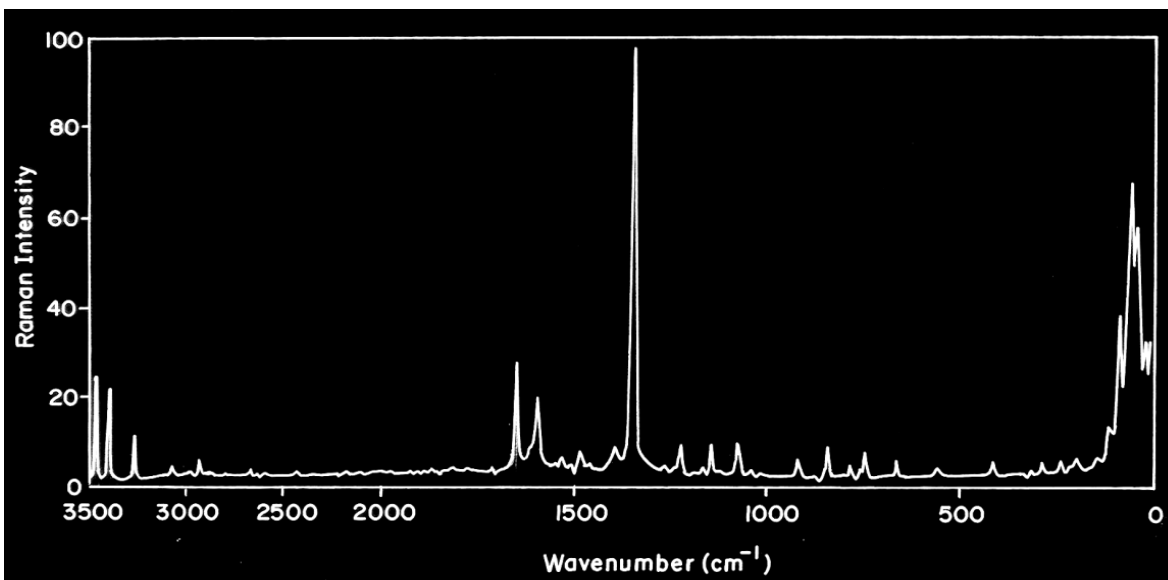
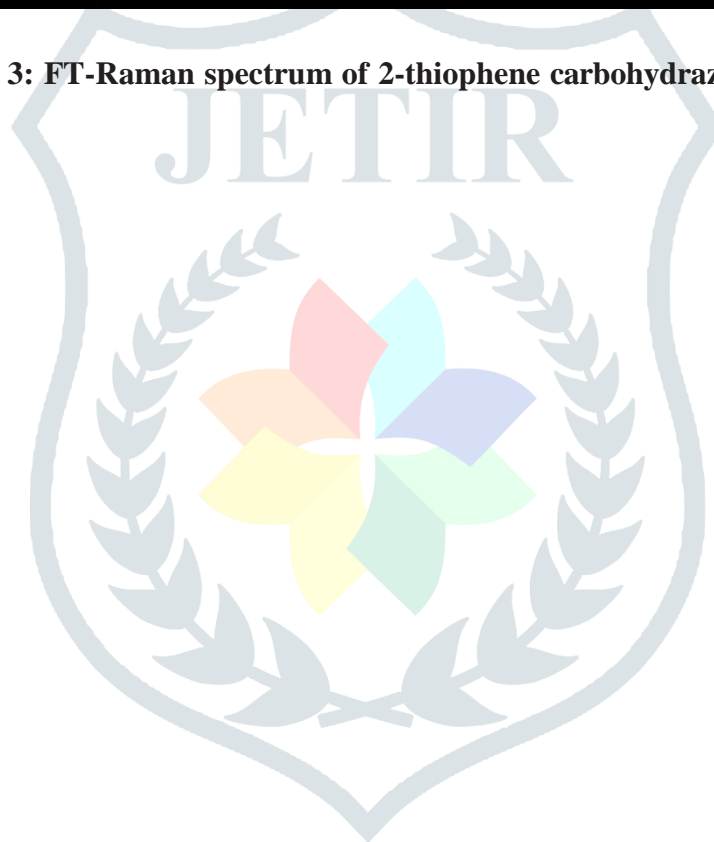


Fig. 3: FT-Raman spectrum of 2-thiophene carbohydrazide





**Table 1: Optimized geometrical parameters of 2-thiophene carbohydrazide obtained by HF/6-31+G(d,p) and B3LYP/6-31+G(d,p) methods with experimental values.**

Bond length	Value(Å)		Expt <sup>a</sup>	Bond Angle	Value (°)		Expt <sup>a</sup>	Diheadral Angle	Value (°)	
	HF/6-31+G(d,p)	B3LYP/6-31+G(d,p)			HF/6-31+G(d,p)	B3LYP/6-31+G(d,p)			HF/6-31+G(d,p)	B3LYP/6-31+G(d,p)
C1-S2	1.7912	1.3427	1.385	S2-C1-C5	111.3253	112.4886	----	S5-C1-C2-C3	0.8079	0.0107
C1-C5	1.3509	1.7787	1.843	S2-C1-C9	119.0208	127.9879	----	C9-C1-S2-C3	179.0852	180.0045
C1-C9	1.4707	1.0652	0.93	C5-C1-C9	129.6265	119.5235	----	S2-C1-C5-C4	-0.7511	180.0028
S2-C3	1.7779	1.4334	1.379	C1-S2-C3	89.3838	112.9867	----	S2-C1-C5-H6	177.8083	-0.0035
C3-C4	1.3473	1.0682	0.93	S2-C3-C4	112.4274	123.7673	----	C9-C1-C5-C4	-178.7954	-0.0065
C3-H8	1.0674	1.3491	1.377	S2-C3-H8	119.7926	123.246	----	C9-C1-C5-H6	-0.236	-179.9993
C4-C5	1.4373	1.0674	0.93	C4-C3-H8	127.7797	114.6134	----	S2-C1-C9-O10	-16.383	-0.0106
C4-H7	1.0705	1.8032	1.843	C3-C4-C5	112.9769	124.1627	119.5	S2-C1-C9-N11	163.2873	-180.0023
C5-C6	1.0715	1.4714	1.437	C3-C4-H7	123.6746	121.2239	119.5	C5-C1-C9-O10	161.5336	-180.0044
C9-O10	1.2304	1.2324	1.229	C5-H4-H7	123.3481	110.5083	----	C5-C1-C9-N11	-18.7961	0.0039
C9-N11	1.3552	1.357	1.365	C1-C5-C4	113.8791	121.2032	----	C1-S2-C3-C4	-0.6855	0.0054
N11-H12	0.9888	0.9923	0.86	C1-C5-H6	123.7359	128.2884	----	C1-S2-C3-H8	179.461	180.0061

N11-N13	1.3919	1.3792	1.37 2	C4-C5-H6	122.3687	89.403	----	S2-C3-C4-C5	0.407	-180.0027
N13-H14	0.9978	0.9924	----	C1-C9-O10	121.7375	119.9605	121. 7	S2-C3-C4-H7	- 179.3551	-0.0019
N13-H15	0.9974	0.9924	----	C1-C9-N11	116.7133	121.6954	115. 7	H8-C3-C4-C5	- 179.7538	0.0005
				O10-C9-N11	121.5484	118.3441	122. 5	H8-C3-C4-H7	0.4841	-180.0003
				C9-N11-H12	122.4174	115.1825	121	C3-C4-C5-C1	0.3223	-0.0116
				C9-N11-N13	122.1048	124.365	121	C3-C4-C5-H6	- 178.3484	-180.0126
				H12-N11-N13	115.223	120.4525	118. 1	H7-C4-C5-C1	179.9961	-180.0107
				N11-N13-H14	112.221	114.527	----	H7-C4-C5-H6	1.4146	-0.0117
				N11-N13-H15	112.1134	114.5214	----	C1-C9-N11-H12	-8.2837	179.995
				H14-N13-H15	112.2112	115.2814	----	C1-C9-N11-N13	177.7952	0.0115
								O10-C9-N11-H12	171.3873	-0.006
								O10-C9-N11-N13	-2.5338	-179.9894
								C9-N11-N13-H14	59.7478	111.7919
								C9-N11-N13-H15	-67.6097	-111.8132
								H12-N11-N13-H14	- 114.5818	-68.1907
								H12-N11-N13-	118.0621	68.2042

								H15		
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<sup>a</sup> Refer the ref. [13,14].



**Table 2:** Vibrational assignments of fundamental modes of 2-thiophene carbohydrazide along with calculated frequencies and normal mode descriptions (characterized by TED) based on quantum mechanical force field calculations using HF and B3LYP methods.

Modes	Symmetry Species	Observed fundamentals (cm <sup>-1</sup> )		Calculated fundamentals(cm <sup>-1</sup> )				Assignment with TED %
				HF/6-31+G(d,p)		B3LYP/6-31+G(d,p)		
		FT-IR	FT-Raman	Unscaled	Scaled	Unscaled	Scaled	
1	A	3412	-	3941	3419	3904	3419	NH <sub>2</sub> ass(100)
2	A	3352	-	3879	3361	3826	3359	NH <sub>2</sub> ss(100)
3	A	3323	-	3805	3329	3770	3328	□NH(91)
4	A	3284	-	3483	3291	3431	3290	□CH(82)
5	A	3259	-	3456	3262	3403	3267	□CH(85)
6	A	3237	-	3428	3244	3377	3244	□CH(84)
7	A	1686	-	1876	1693	1759	1694	□C=O(76)
8	A	1630	-	1796	1637	1702	1637	NH <sub>2</sub> sciss(62)
9	A	1685	-	1764	1692	1681	1692	□CC(71)
10	A	1612	-	1649	1618	1587	1621	NH <sub>2</sub> rocking(59)
11	A	1499	-	1621	1507	1494	1508	□C-C(72)
12	A	-	1486	1537	1493	1453	1477	□C-C(79)
13	A	1471	-	1498	1478	1380	1479	□C-S(69)
14	A	1382	-	1411	1391	1267	1388	□C-S(71)
15	A	-	1365	1392	1372	1249	1372	□C-N(68)
16	A	-	1284	1314	1293	1243	1291	□C-CO(59)
17	A	1232	-	1227	1230	1126	1239	◆CH(64)
18	A	-	1229	1145	1221	1084	1235	◆NH(61)

19	A	-	1178	1143	1169	1039	1185	□N-NH <sub>2</sub> (56)
20	A	1117	-	1131	1124	939	1126	◆CH(68)
21	A	1089	-	1069	1081	867	1081	◆CH(74)
22	A	-	935	915	928	850	927	Rbend 1(51)
23	A	926	-	870	919	747	919	□CH(56)
24	A	874	-	845	869	731	867	□CH(47)
25	A	851	-	794	847	699	842	Rbend 2(49)
26	A	749	-	766	755	661	757	□CH(63)
27	A	-	696	712	703	659	685	□NH(68)
28	A	667	-	711	672	560	659	◆C=O(72)
29	A	603	-	676	611	554	594	◆C-NN(56)
30	A	-	597	627	604	471	589	NH <sub>2</sub> wag (46)
31	A	-	483	577	492	410	472	NH <sub>2</sub> twist (49)
32	A	451	-	499	459	399	445	□C=O (59)
33	A	-	273	414	283	373	284	◆C-CO(64)
34	A	-	261	379	269	252	259	◆N-NH <sub>2</sub> (42)
35	A	-	241	311	248	166	233	tRtorsional 1 (47)
36	A	-	197	204	201	132	189	tRtorsional 2 (51)
37	A	-	155	194	163	103	146	□N-NH <sub>2</sub> (51)
38	A	-	126	153	132	76	118	□C-CO (53)
39	A	-	109	40	101	46	98	□CNN (52)

**Abbreviation:** y - stretching; as - asymmetric stretching; ss - symmetric stretching; ◆ - in-plane-bending; □ - out-of-plane bending; ipw - in-plane wagging; opw - out-of-plane wagging; t - torsion.

**Table 3:** The calculated thermodynamic parameters of 2-thiophene carbohydrazide employing HF/6-31+G(d,p) and B3LYP/6-31+G(d,p) methods.

Thermodynamic parameters(298k)	HF/6-31+G(d,p)	B3LYP/6-31+G(d,p)
Total thermal energy (kcal mol <sup>-1</sup> )	81.063	74.827
Heat capacity at constant volume, c <sub>v</sub> (kcal mol <sup>-1</sup> k <sup>-1</sup> )	28.801	27.113
Entropy S (kcal mol <sup>-1</sup> k <sup>-1</sup> )	89.313	84.291
Vibrational energy, E <sub>vib</sub> (kcal mol <sup>-1</sup> )	79.286	73.050
Zero- point vibrational Energy, E <sub>0</sub> (kcal mol <sup>-1</sup> )	76.12763	70.39497
Rotational constants(GHz)		
A	2.46925	2.46925
B	1.19772	1.19772
C	0.81018	0.81018

**Table 4: Mulliken Atomic Charges of 2-thiophene carbohydrazide at HF/6-31+G(d,p) and B3LYP/6-31+G(d,p) methods.**

Atom s	HF/6- 31+G(d,p)	DFT/6- 31+G(d,p)
C1	-0.271093	-0.318160
C2	-0.555288	-0.310108
C3	0.194868	-0.080755
C4	0.100111	0.088898
S5	0.262949	0.367884
H6	0.250059	0.202858
H7	0.253908	0.192015
H8	0.293125	0.224701
C9	0.197138	0.173133
O10	-0.635080	-0.503616
N11	-0.376379	-0.201326
H12	0.466553	0.403623
N13	-0.986131	-1.003495
H14	0.402635	0.382181
H15	0.402625	0.382168

**Table 5: APT Charge Distribution of 2-thiophene carbohydrazide at HF/6-31+G(d,p) and B3LYP/6-31+G(d,p) methods.**

Atomic numbers	HF/6-31+G(d,p)	B3LYP/6-31+G(d,p)
C1	0.030041	-0.024749
C2	-0.205375	-0.167903
C3	0.033041	-0.008408
C4	-0.257602	-0.202395
S5	-0.030510	0.017589
H6	0.089861	0.076685
H7	0.072111	0.061923
H8	0.112235	0.100174
C9	1.519375	1.277376
O10	-1.015998	-0.857337
N11	-0.631147	-0.483430
H12	0.211969	0.178661
N13	-0.338236	-0.332004
H14	0.205117	0.181906
H15	0.205118	0.181912



Table 6:NBO analysis of 2-thiophene carbohydrazide by B3LYP/6-31+G(d,p) method.

Donor(i)	ED(i) (e)	Acceptor(j)	ED(j) (e)	E(2) <sup>a</sup> (kJ mol <sup>-1</sup> )	E(i)- E(j) <sup>b</sup> (a.u.)	F(I, j) <sup>c</sup> (a.u.)
n(C1-C2)	1.8899 0	n*(C3-C4)	0.0168 6	29.19	0.56	0.11 8
n(C3-C4)	1.86185	n*(C1-C2)	0.2064 3	21.07	0.55	0.09 7
		n*(C9-O10)	0.2614 5	32.14	0.53	0.12 1
n*(C9-O10)	0.2614 5	n*(C3-C4)	0.0168 6	159.11	0.02	0.10 1
cr(C2-H7)	1.9763 9	cr*(C1-S5)	0.0245 8	7.15	1.08	0.07 8
cr(C3-H8)	1.9735 8	cr*(C4-S5)	0.0300 4	8.90	1.05	0.08 7
LP2 S5	1.73324	n*(C1-C2)	0.2064 3	34.27	0.50	0.11 9
		n*(C3-C4)	0.0168 6	28.84	0.51	0.10 9
LP2 O10	1.91070	cr*(C4-C9)	0.0542 0	22.70	1.09	0.14 2
		cr*(C9-N11)	0.0560 8	27.91	1.13	0.16 0
LP1 N11	1.78917	n*(C9-O10)	0.2614 5	92.63	0.56	0.20 6
		cr*(N13-H14)	0.0133 4	8.71	1.09	0.09 1
		cr*(N13-H15)	0.0133 4	8.71	1.09	1.09
LP1 N13	1.9625 3	cr*(N11-H12)	0.0235 7	12.28	1.16	0.10 7

<sup>a</sup> E<sup>(2)</sup> means energy of hyperconjugative interactions.

<sup>b</sup> Energy difference between donor and acceptor i and j NBO orbitals.

<sup>c</sup> F(i, j) is the Fock matrix element between i and j NBO orbitals.