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Spectroscopic Investigation, HOMO-LUMO analysis and DFT studies on Acetone Thiosemicarbazone

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ABSTRACT

The present investigation is aimed at the experimental and theoretical studies on molecular structure, vibration spectra of Acetone Thiosemicarbazone ($C_4H_9N_3S$) were studied. The FT-IR and FT-Raman spectra were recorded. The molecular geometry and vibrational frequencies of the ground state were calculated by using Hartree-Fock and Density functional methods (B3LYP) with 6-311, 6-311++G(d,p) basis sets. Comparison of the observed fundamental vibrational frequencies of Acetone Thiosemicarbazone by HF and DFT method. The electric dipole moment (μ) and the first hyperpolarizability (β) values of the investigated molecule were also computed.

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Introduction

Semicarbazones and Thiosemicarbazone have been investigated due to interest in their co-ordination behaviour analytical applications [1] and biological properties such as antibacterial [2], semicarbazones [3,4] and Thiosemicarbazone [5,6] are biologically important nitrogen and oxygen/sulphur donor ligands. Semicarbazones of aromatic and unsaturated carbonyl compounds have anticonvulsant properties and their advantage over the analogues thiosemicarbazones is their lower neurotoxicity [7] the alkylated sulphur atom remains uncoordinated on complexation. These characteristics and properties make these compounds attractive for the preparation of variety of new complexes. In recent years, among the computational methods calculating the electronic structure of molecular systems, DFT and HF have been a favourite one due to its great accuracy in reporting the experimental values. The success of quantum chemical methods in predicting a large number of important parts of their emergence as a legitimate tool for many chemical problems

Synthesis & Experimental details

Acetone Thiosemicarbazone (ATS) were synthesised in laboratory by refluxing acetone (0.05 mol) and thiosemicarbazide (0.05 mol) in ethanol medium with constant stirring for 2 hrs. The solvent was evaporated under reduced pressure and unreacted thiosemicarbazide was separated from the mixture by washing with ethanol. The yellow precipitated compound was dried in vacuum in desiccators.

The FT-IR spectrum was recorded on a Perkin Elmer infrared spectrometer with KBr pellets. The FT-Raman spectrum was obtained on a Bruker RFS 100/s instrument. For excitation of the spectrum, the emission of ND:YAG laser was used (excitation wavelength 1064 nm, laser power of 100 mW, resolution 4 cm⁻¹, number of scans 50 and measurement on solid sample).

Computational details

The molecules under investigation have been analysed with density functional theory (DFT) employing Becke's three

parameter hybrid exchange functional B3LYP and HF. All the calculations were performed using Gaussian 09 program [8]. The DFT was also used to calculate the dipole moment, mean and the first static hyperpolarizability (β) of the title compound.

Results and Discussion

ATS is a substituted semicarbazone with two different functional groups such as methyl and amine group in semicarbazone. The optimized geometry of ATS which is performed by HF method and B3LYP methods with atoms numerically is shown in figure 1. The optimized bond length, bond angle is calculated by DFT/B3LYP method are consistent with those by HF method (Fig 2). The available X-ray diffraction values of similar are also given in Table 1 for comparison. The theoretical results are almost comparable with the reported structure parameters of similar type of compound. The experimental N-N bond length is reported at 1.380 Å for Acetone Phenyl Semicarbazone. The calculated bond length in our compound are close related with these values. For the title compound bond length C=N as 1.258 to 1.281 shows typical double bond characterization of our C=N as 1.348 to 1.379 or shorter than normal C-N which is about 1.48 Å, this showing of C-N bonds reveals the effect of resonance in this part of the molecule. For the title compound this bond angle by DFT method as C-N-N as 118.1 to 122.4 and N-C-N is 111.4 and N-C-N is 116.0.

Vibrational Analysis

The maximum number of potentially active observable fundamentals of a non-linear molecule which contains N atoms is equal to (3N-6), apart from three translational and three rotational degrees of freedom [9]. Hence, ATS molecule, which was planar, has 17 atoms with 45 normal modes of vibrations. All vibrations are active both in Raman and infrared absorptions. The detailed vibrational assignment of the experimental wavenumbers is based on normal mode analyses and a comparison with the experimental values. The observed IR and Raman bands and calculated wave numbers and

assignments are given in Table 2. The experimental and theoretical spectra are shown in figure 3 and 4.

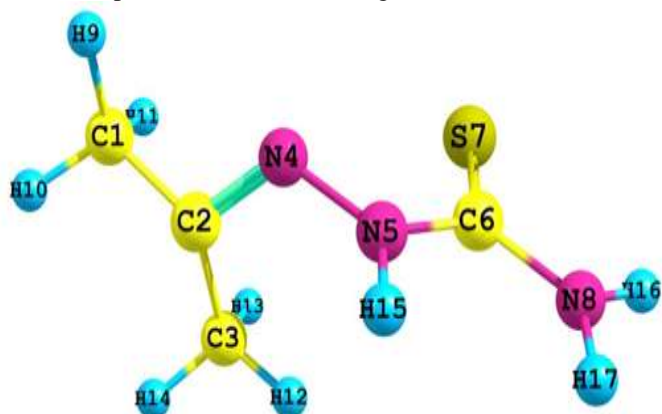


Fig. 1. The theoretical optimized possible geometric structure with atoms numbering of acetone thiosemicarbazone

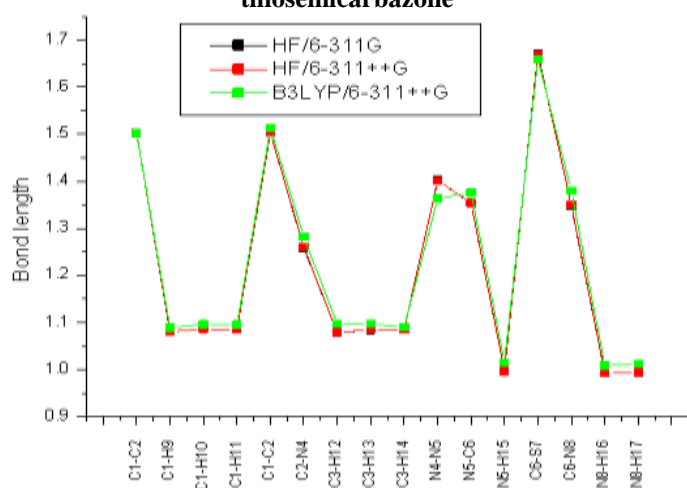


Fig.2. Bond length differences between theoretical (HF and DFT) approaches

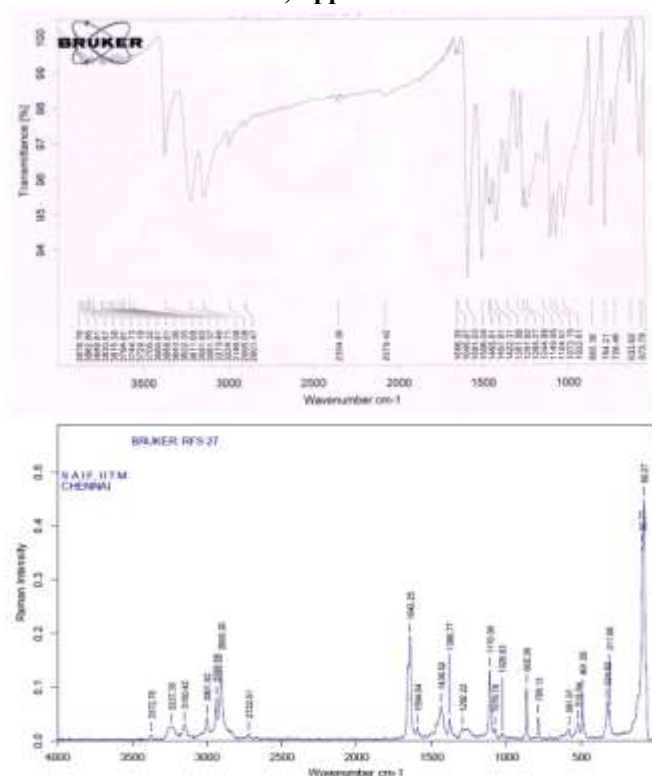
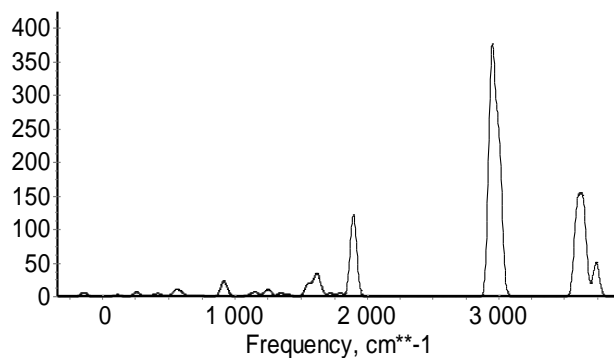


Fig.3. Experimental FT IR and Raman Spectrum for ATS

HF/6-311++G



HF/6-311++G

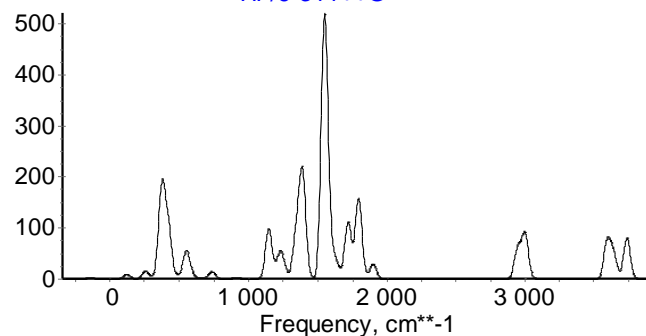


Fig. 4. Theoretical FTIR and FT Raman spectrum for ATS C=N Stretching

The C=N stretching skeletal bonds 25 are observed in the range 1650-1550 cm^{-1} . According to Socrates [10] The C=N stretching for semicarbazones in the range 1655-1640 in IR spectrum. Ferraz et al[11] Reported C=N at 1643 for Thiosemicarbazone derivatives. For the title compound sharp band at 1656 cm^{-1} in IR and 1643 cm^{-1} in Raman coincides well with the experimental values can be contributed to the characteristic C=N group. The theoretical wave number of this band at 1632 cm^{-1} is coincide with experimental value.

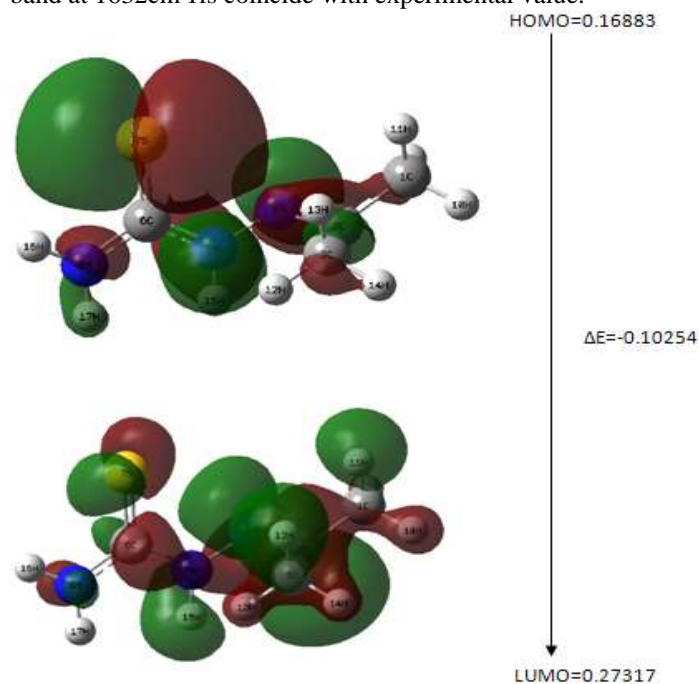


Fig.4. The molecular orbitals and energies for the HOMO and LUMO of the title compound

C-N Stretching

The C-N stretching vibration [12] coupled with δ NH active in this region $1275 \pm 25 \text{ cm}^{-1}$ El- Shahawy et.al[10] 1320 cm^{-1} in the IR spectrum as this C-N mode. In present case the band at 1265 cm^{-1} in Raman spectrum is assigned in this mode the DFT calculations gives the corresponding bands at 1260 cm^{-1}

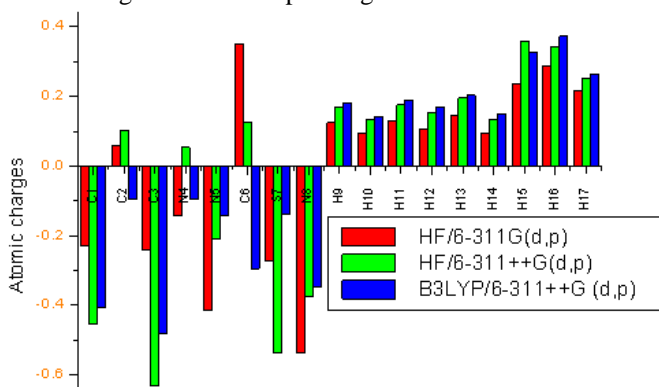


Fig.5. Comparative graph of Mulliken atomic charges of Acetone Thiosemicarbazone

N-N Stretching

The N-N stretching has been reported at 1151 cm^{-1} by crane et.al[13] In the present case the band is observed $1110, 1104 \text{ cm}^{-1}$ in both IR and Raman spectra and 1038.11 cm^{-1} DFT is assigned to the N-N is reported.

CH₃ Stretching

In the spectra of methyl group overlap of the region in which both asymmetric stretching CH₃ absorb with weak band at $(2985 \pm 25 \text{ cm}^{-1}, 2970 \pm 30 \text{ cm}^{-1})$ the computed wave numbers of modes corresponding to CH₃ groups are $2962, 3003 \text{ cm}^{-1}$. The symmetrical stretching mode is expected in the range $2920 \pm 80 \text{ cm}^{-1}$ in which all the three C-H bonds extending and contracting in phase[14] The bands present in experimental 2901 cm^{-1} (IR) and 2905.20 cm^{-1} in Raman are assigned these particular modes. Two bending vibrations accrue in methyl group

NH₂ Stretching

The NH₂ asymmetric stretching vibrations [14] gives rise to a strong band in the region $3390 \pm 60 \text{ cm}^{-1}$ and the symmetric NH₂ stretching in the region $2985 \pm 25 \text{ cm}^{-1}$ with some what weaker intensity for this compound. The NH₂ bending is observed at 1361 cm^{-1} in IR 1380 cm^{-1} in Raman theoretically NH₂ is reported at 1409 cm^{-1} in HF 1319 cm^{-1} in DFT. The amide band absorbing in the region $775 \pm 45 \text{ cm}^{-1}$ is assigned to NH₂ out of plane twist and wagging mode ρ NH₂ wag is expected in the region[15] $670 \pm 60 \text{ cm}^{-1}$. In which all the three C-H bonds extend and contract in phase[17] The bands seen at 737 cm^{-1} in HF 670 cm^{-1} in DFT and in experimental 784.21 cm^{-1} and 786.13 cm^{-1} in Raman are assigned as these modes.

N-H Stretching

The NH stretching vibration [17] appears as strong and broad band in the region $3390 \pm 60 \text{ cm}^{-1}$. In the present study the NH stretching band appeared as doublet at $3146.08, 3224.71 \text{ cm}^{-1}$ in the IR region owing to the Davydov coupling between the neighbouring units. The splitting in IR spectrum is due to Strong inter molecular hydrogen bonding. A similar type of splitting observed in acetanilide [16, 17] and N methyl acetamide [17] in the stretching band is attributed to the Davydov splitting.

C=S Stretching

The identification of C=S stretching vibration is assigned to 1022.61 cm^{-1} in IR spectra and 1029.83 cm^{-1} in Raman spectra. The calculated values are 922.05 cm^{-1} in HF and 874.3861 cm^{-1} in DFT method. There bands appear consistently in the region of 1140 cm^{-1} to 940 cm^{-1} in the IR spectrum because of mixed vibrations of -N-C=S moiety[18]

Mulliken atomic charges

Mulliken atomic charge calculation has an important role in the application of quantum chemical calculation to molecular system because of atomic charge affects dipole moment electronic structure, molecular systems. The total atomic charges of acetone thiosemicarbazone are obtained by Mulliken population analysis is shown in Table 4. The results shows that substitution of methyl group in the thiosemicarbazone leads to the redistribution of electron density. The charge distribution shows all the hydrogen atoms and carbon atoms in few sets are positively charged where as the magnitude of the carbon atomic charges were found to be both positive and negative values the charge of N is negative in most of the basis sets however the highest value is $-0.5359e$. The sulphur atom has negative values only in all basis sets due to electron withdrawing nature. The comparative graph for Mulliken charges is shown in figure 5.

Thermo dynamical properties

The values of some thermo dynamical parameters (Zero point vibrational energy, Thermal energy, Specific heat capacity rotational constants, entropy etc.) of ATS at 298.15 K in ground state are listed in Table 5. Dipole moments reflects the molecular charge distribution and is given as 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 centre of positive negative charges Dipole moments are strictly determined for neutral molecules. Scale functions have been recommended for an accurate prediction in determining the zero point vibrational energy and entropy $S_{\text{vib}}(T)$ The variation in zero point vibration energy seems to be significant. ATS molecule has a high dipole moment value (5.38 Debye) which increases its ability to interact with surrounding matrix. Therefore ATS molecule is a prominent structure for many applications.

Hyperpolarizability

The hyper polarizability is calculated using HF method on the basis of finite field approach. Calculated parameters are listed in Table 3, it is well known that higher values of dipole moment and first hyperpolarisability are more important for NLO properties The calculated value of first hyperpolarizability β of title compound is $67.160 \times 10^{-33} \text{ esu}$. Therefore we conclude that the title compound is an attractive object for future studies of Non linear optical properties.

Frontier molecular Orbital's (FMOs)

The highest occupied molecular orbital's (HOMO) and the lowest lying unoccupied molecular orbital's (LUMO) are named as Frontier molecular orbital's (FMO) The FMO play an important role in the optical and electric properties [18] as well as in quantum chemistry and UV visible spectra. The HOMO-LUMO energy gap of ATS have been calculated by using ab-initio HF/6-31G levels is Shown in Fig 6. reveals that the energy gap reflect the chemical activity of the molecule are presented. LUMO as an electron acceptor represents in the electron ability to obtain an electron; HOMO represents to donate an electron. It is clear that the HOMO-LUMO gap is 0.10254 it reveals that the molecule is soft and easily reactive.

Table 1: Optimized geometrical parameters of Acetone ThioSemi Carbazone, bond length (Å), bond angles (°).

PARAMETERS	HF/6-311G	HF/6-311++G	B3LYP/ 6-311++G	Experimental value
C1-C2	1.5032	1.5032	1.5021	1.082
C1-H9	1.0803	1.0805	1.0892	
C1-H10	1.0866	1.0866	1.0961	
C1-H11	1.0863	1.0864	1.0959	
C1-C2	1.503	1.5032	1.5131	1.380-1.390
C2-N4	1.2588	1.2598	1.2818	
C3-H12	1.079	1.0791	1.0966	
C3-H13	1.0844	1.0845	1.0967	
C3-H14	1.0855	1.0856	1.0899	1.319
N4-N5	1.4021	1.4019	1.3636	
N5-C6	1.3532	1.3538	1.3759	
N5-H15	0.9966	0.9968	1.0149	
C6-S7	1.6711	1.669	1.6585	1.286
C6-N8	1.3487	1.3501	1.3794	
N8-H16	0.9922	0.9926	1.0086	
N8-H17	0.9944	0.9945	1.012	
BOND ANGLE				
C2-C1-H9	110.3348	110.5128	110.2285	118.6
C2-C1-H10	110.2473	110.1757	110.7009	
C2-C1-H11	109.5844	109.5325	110.6609	
H9-C1-H10	109.7352	109.7017	109.11	
H9-C1-H11	109.2944	109.284	109.1027	120
H10-C1-H11	116.3944	116.3395	118.2417	
C1-C2-N4	116.0294	116.0823	116.9371	
C3-C2-N4	127.5756	127.578	124.8211	
C2-C3-H12	112.319	112.4129	111.4789	121.2
C2-C3-H13	109.0555	109.0473	111.573	
C2-C3-H14	109.1645	109.1003	110.9012	
H12-C3-H13	108.5185	108.518	107.7479	
H12-C3-H14	109.586	109.5622	107.5197	118.6
H13-C3-H14	108.1039	108.1043	107.4196	
C2-N4-N5	116.9066	117.0176	118.1195	
N4-N5-C6	122.4847	122.4137	121.7551	
N4-N5-H15	109.0203	109.0052	119.7387	121.2
C6-N5-H15	113.9494	114.129	117.4596	
N5-C6-S7	125.6316	125.5764	125.9417	
N5-C6-N8	113.1206	113.2836	111.5346	
S7-C6-N8	121.2446	121.1376	122.4898	121.2
C6-N8-H16	116.5276	116.622	113.8994	
C6-N8-H17	120.4026	120.6776	118.8365	
H16-N8-H17	117.3471	117.4227	115.0162	

*Similar type of compound

Table 2. Comparison of the experimental (FT-IR and FT-Raman) and theoretical harmonic wave numbers (cm⁻¹) of Acetone Thiosemicarbazone calculated by HF, B3LYP with 6-311++G (d, p) basis set

Modes No	Experimental		6-311++G (d,p)	B3LYP /6-311++G (d,p)	Assignment
	IR	Raman			
1			3729.49	3664.27	N-H ₂ Asymmetric Stretching
2			3633.36	3554.05	N-H Stretching
3	3373.46	3372.76	3586.61	3517.70	N-H ₂ Symmetric Stretching
4	3373.46	3372.76	3003.93	2931.12	CH ₃ Symmetric Stretching
5	3224.71	3237.35	3001.14	2928.32	C-H ₂ Asymmetric Stretching
6	3146.08	3001.92	2991.09	2922.12	C-H ₂ Asymmetric Stretching
7	2995.08	2938.69	2983.54	2914.71	C-H ₃ Asymmetric Stretching
8	2901.47	2905.20	2942.56	2865.15	C-H ₃ Symmetric Stretching
9	2354.36		2935.76	2859.15	C-H ₃ Symmetric Stretching
10	2079.42		1897.44	1790.50	C=N Stretching
11	1656.35	1643.25	1795.86	1627.81	N-H ₂ In plane Bending
12	1645.87		1719.48	1558.82	N-H In plane Bending
13	1591.53	1594.04	1648.29	1524.66	C-H ₂ In Wagging
14	1506.04		1625.61	1502.94	C-H ₃ Out of plane Bending
15	1465.91	1436.52	1617.27	1492.28	C=S Out plane Bending
16			1609.31	1483.84	C-H ₂ In Plane Bending
17			1588.67	1478.53	C-H ₃ In plane Bending
18	1457.81		1584.72	1446.79	C-H ₃ In plane Bending
19	1422.31		1550.11	1435.22	C-H ₃ In plane Bending
20	1361.56	1380.77	1407.01	1311.61	N-C-H In plane Bending
21	1297.82	1292.22	1387.97	1283.89	C-H ₃ Out of plane Bending
22	1265.27		1343.48	1252.33	N-N Stretching
23	1244.88		1254.36	1142.94	C-H ₃ Out of plane Bending
24	1149.95	1110.06	1225.26	1119.96	C-H ₃ Out of plane Bending
25	1104.51		1156.11	1055.59	C-H ₃ Out of plane Bending
26	1073.15	1076.73	1147.28	1038.27	N-H ₂ Out of plane Bending
27	1022.61	1029.83	1100.22	1000.72	C-H ₃ Rocking
28	862.36	865.39	922.05	870.52	C=S Stretching
29	784.21	786.13	905.09	866.59	C-H ₃ Out of plane Bending
30	726.46		737.43	673.31	N ₂ -H Out of plane Bending

31	633.62		718.04	585.34	C-N, N-H Out of plane Bending
32	573.79	581.91	667.94	554.72	C-C-C In plane bending
33			591.51	526.79	NH ₂ Out plane bending
34		519.84	554.44	453.87	C-H ₃ Out of plane Bending
35		491.50	519.23	439.57	C-H ₃ Out of plane Bending
36			495.40	425.87	C-H ₃ In Plane Bending
37			486.44	405.58	N-H-H In Plane Bending
38			425.11	366.05	C-H ₃ In Plane Bending
39			398.18	352.66	C-N-N In Plane Bending
40		324.82	378.30	262.46	C-H ₃ In Plane Bending
41			329.13	91.71	CH ₃ In plane bending
42		90.77	257.59	21.79	CH ₃ -NH-C=S Out plane bending
43			124.35	-104.86	NH ₂ Out plane bending
44			105.11	-235.70	NH Out plane bending
45			-140.31	-376.52	NH Out plane bending

Table 4. First order hyperpolarizability of Acetonethiosemicarbazone

First order hyperpolarizability (a.u)	
β_{xxx}	5.8350
β_{xxy}	-4.4455
β_{xyy}	1.1575
β_{yyy}	-1.6199
β_{xxz}	7.3998
β_{xvz}	-2.1229
β_{vvz}	-3.2305
β_{xzz}	-6.0643
β_{vzz}	1.6453
β_{zzz}	2.1583
β_{tot}	7.7741 a.u = 67.160 x 10 ⁻³³ esu

Table 5. Mulliken atomic charges of Acetone Thiosemicarbazone

Atoms	HF/6-311G(d,p)	HF/6-311++G(d,p)	B3LYP/6-311++G(d,p)
C ₁	-0.2288	-0.452317	-0.406465
C ₂	0.056849	0.103364	-0.094133
C ₃	-0.242768	-0.62959	-0.481602
N ₄	-0.143798	0.05348	-0.094432
N ₅	-0.413985	-0.209511	-0.140493
C ₆	0.348937	0.127084	-0.294136
S ₇	-0.272907	-0.536688	-0.139819
N ₈	-0.535955	-0.376187	-0.345554
H ₉	0.124036	0.169424	0.181948
H ₁₀	0.093818	0.133603	0.140208
H ₁₁	0.130558	0.174963	0.188532
H ₁₂	0.104637	0.155066	0.169581
H ₁₃	0.1466	0.195717	0.203316
H ₁₄	0.094661	0.13452	0.147793
H ₁₅	0.234381	0.35981	0.327741
H ₁₆	0.286435	0.344155	0.372108
H ₁₇	0.217303	0.253107	0.265408

Table 6. The calculated thermo dynamical parameter of Acetone Thiosemicarbazone

Basis Set	HF/ 6-311G(d,p)	HF/ 6-311++G(d,p)	B3LYP/ 6-311++G(d,p)
Zero point energy (Kcal/Mol)	91.58787	91.60880	91.60880
Rotational constant	0.90973	0.90973	0.90973
Rotational temperature (K)	0.04366	0.04366	0.04366
Energy(E)			
Translational	0.889	0.889	0.889
Rotational	0.889	0.889	0.889
Vibrational	94.615	94.624	88.189
Total	96.393	96.401	89.966
Specific heat (C _w)			
Translational	2.981	2.981	2.981
Rotational	2.981	2.981	2.981
Vibrational	22.915	22.889	20.594
Total	28.877	28.850	26.556
Entropy(S)			
Translational	40.524	40.524	40.524
Rotational	29.053	29.053	29.053
Vibrational	16.801	16.713	14.120
Total	86.378	86.290	83.697
Dipole moment (Debye)	5.99	5.83	5.36

Conclusion

A complete vibrational analysis of ATS are performed by HF and DFT-B3LYP methods with 6-311++G (d, p) basis sets. The influence of methyl group, amino group and carbon sulphur bond to the vibrational frequencies of the title compound were discussed. The N and S atoms negative charge shows that electron withdrawing nature. The HOMO-LUMO gap is as small 0.10254 it reveals that is a easily reactive compound. The first order hyper polarizability values are 67.160×10^{-33} esu. This indicates that the title compound is an attractive object for future studies of Non linear optical properties.

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