Ab intio and DFT study of hydroxy amino acids: A nano scale study

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The molecular structures of serine, threonine and tyrosine molecules in its neutral form have been optimized using ab initio quantum mechanical calculations and DFT level of theory. We have determined the molecular structures, Dipole moments, Polarizabilities, Rotational constants and Vibrational frequencies of these selected three hydroxy amino acids. Different basis sets were also tested and compared to determine which basis set is the most efficient to model these particular amino acids. The addition of polarization function leads to longer bond length and shorter bond angles. The changes in different stretching vibrational modes of O-H groups have been analyzed from serine to tyrosine.

Keywords: Ab-initio, serine, threonine and tyrosine, Density Functional Theory, Vibrational frequencies, Infrared spectra.

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Introduction:

Serine (2-amino-3-hydroxypropane) is one of the aliphatic amino acid and its structure and molecular dynamics has been the subject of wide interest for many years. Amino acids often acquire zwitterionic form in liquid and solid phases. This is confirmed by experimental studies [1-3]. The Raman and IR spectra of serine are reported in a number of research papers [4-8]. The structure of L-serine has been studied by X-ray diffraction [9-11] and neutron diffraction method [12]. All these studies reveal that serine is in its zwitterion form in the crystals. Ab initio studies in gas phase and vibrational analysis of several amino acids have been carried out by several workers [13-16]. Calculations regarding protonation [17-19] and low energy conformations [20, 21] of serine have also been reported. It is shown that the most favourable site for protonation in serine is at the nitrogen atom of the amino group. In all these studies, optimizations were carried out only at RHF level without introducing electron correlation effect.

Threonine (2-amino-3-hydroxy-butanecarboxylic acid) is a member of aliphatic hydroxy amino acid. It is an important amino acid found in several proteins of human beings such as γ-globulin, β-lactoglobulin, hemoglobin, insulin, silk fibroin and among others [22]. Investigation of threonine is relevant for the physical point of view of both owing to the possibility to observe the behaviour of a system where the hydrogen bond plays a fundamental role [23-25] and the technological importance of a material which shows second harmonic conversion efficiency greater than 1 relative to potassium dihydrogen phosphate [26]. Requirements for Threonine appear to decrease with age and increase with stress. It is necessary for the formation of tooth enamel, elastin and collagen which are needed for both healthy skin and wound healing. It also plays a role in preventing fat from accumulating in the liver. Threonine has been investigated extensively by various authors [27-32]. Infrared (I.R.) absorption measurements and polarized Raman Scattering results for L-threonine at room temperature and assignments of some internal modes are also reported by Freire et al. [33]. Schäfer and coworkers [28] considered gaseous Threonine on the basis of favorable intramolecular interaction and yielded possible conformer. The ionization energies of four conformer of threonine has been calculated by Powis et al [29] and compared with their synchrotron radiation photoelectron spectroscopy experiment. The orbital dependent vertical ionization energies of four threonine conformer have been studied by Dehareng et al [30] using the outer valence green's function (OGVF) technique.

Tyrosine is a nonessential amino acid that is synthesized in the body from phenylalanine. As a building block for several important brain chemicals, tyrosine is needed to make epinephrine, norepinephrine, serotonin, and dopamine, all of which work to regulate mood. Deficiencies in tyrosine, therefore, have been associated with depression. Tyrosine also aids in the production of melanin. Therefore tyrosine may be valuable aid in treating vitiligo and in the function of organs in the body responsible for making and regulating hormones, including the adrenal, thryroid, and pituitary glands. It is also involved in the synthesis of enkephalins, substances that have pain-relieving effects in the body. Low levels of tyrosine have been associated with low blood pressure, low body temperature, and an under active thyroid. Because tyrosine binds unstable molecules called free radicals, it is considered as a mild antioxidant. Thus, tyrosine may be useful for people who have been exposed to harmful chemicals and radiation. Tyrosine in gas phase has been well studied [34, 35]. Earlier, Hameka et al [36] has been reported the ground state (S_0) energy at HF/6-31g level and first singlet excited state (S_1) energy at CIS/6-31G level of theory for tyrosine and also interpreted the absorption and fluorescence spectra reported previously by Teale and Weber [37]. Recently, the structure and conformational behaviour of neutral tyrosine using the experimental technique of matrix-isolation high resolution Fourier Transform Infrared Spectroscopy in combination with DFT/B3LYP/6-31++G** computational quantum chemistry has been carried out by Ramaekers et al [38]. The experimental result of the ultraviolet excitation and fluorescence spectra of tyrosine have been reported earlier [39-41] The work of S. Hill has indicated that the tyrosine molecule may also exhibit phosphorescence under certain conditions [42]. Samuels et al. [43] reported computational results at the CASSCF(6,6)/6-31G level of theory for two lowest singlet state S_0 and S_1 and for the two lowest triplet states T_1 and T_2 of the tyrosine molecule where S_0 being the molecular ground state.

Recently, the three hydroxy amino acids (serine, threonine and tyrosine) have been studied at the Hartree-Fock level of theory based on geometry optimization for one initial structure for each molecule by B. Lakard [31]. We can observe that the amino acids (H_2N-CHR-COOH) studied here only differ by their –R group, which contain a primary alcohol for serine, a secondary alcohol for threonine and a primary aromatic alcohol for tyrosine. Therefore, it can be interesting to compare the physiochemical properties common to these three amino groups. The purpose of this investigation to study the molecular structure, total electronic energy, dipole moments, polarizabilities, rotational constants and vibrational spectra of the three most important hydroxy amino acids (Serine, Threonine and tyrosine). Furthermore, the general assignments of their fundamental frequencies are proposed by ab initio DFT calculation and compared with observed IR spectrum. In present study, electron correlation has been included using the DFT approximations with different basis sets. Density functional theory calculations are already reported to provide excellent agreement with experimental vibrational frequencies for organic compounds, if the calculated frequencies are scaled appropriately [44-50].

Methodology:

Experimental Study:

Hydroxyamino acids (serine, threonine and tyrosine) samples used in the present investigation was obtained from Merck (99% purity) have been used as such without further purification to record the infrared (IR) spectrum in a nujoll mull using a Fourier Transform IR spectrometer (JASCFTIR-5300) with a resolution of 2 cm^{-1} in the range of 400-4000 cm^{-1}. The IR spectrum of the molecules in a K Br pellet was also recorded on a Perkin Elmer RX1, FT-IR spectrometer in the range 450-4000 cm^{-1} with a resolution of 1 cm^{-1}.

Computational Methodology:

The geometry optimizations and frequency calculations have been carried out with the Hartree-Fock [51] and density functional theory (DFT). Here, we have used the hybrid of Becke's non-local three parameter exchange and correlated functional with the Lee- Yang-Parr correlation functional (B3LYP) methods [52] using different basis sets viz; 6-311++G** and Aug-cc-Pvdz for the molecular orbital expansion without imposing any symmetry constraints. The optimized geometries at the B3LYP/6-311++G** level are used as starting geometry for optimization at the DFT/B3LYPAug-cc-Pvdz level of theory. The frequency calculations were carried out at same level of theory as the respective optimization processes using analytic evaluation of the second derivatives of energy with respect to the nuclear displacement. The DFT/B3LYP method has been widely applied to obtain the conformational behaviour, theoretical vibrational frequencies and infra red intensities of amino acids, which are well agreed with the experimental data for alanine [53], glycine [54] Proline [55], tyrosine[56] and valine [57].All calculations in the present work were carried out on a Pentium IV PC using Gaussian 03 [58] suite of ab initio quantum mechanical program.

Results and Discussion:

Geometry and Relative Energies:

The optimized geometrical parameter (i.e. bond lengths, bond angles and dihedral angles) of hydroxyl amino acids (serine, threonine and tyrosine) at RHF and DFT/B3LYP level of theories by employing 6-311++G** and Aug-cc-Pvdz basis sets in gas phase are listed in Tables 1-3and provided as supplement material. Tables 1-3 are not be the part of the paper due to space problem. The experimental values reported earlier by Kistenmacher et al [11] and theoretical estimates made by Friere et al [12] for the L-form of serine are also included in Table 1. The molecular structures of serine, threonine and tyrosine are shown in Figures 1-3. Taking the chiral carbon as being in the plane of the paper [Fig.1] the COOH and COH_3 groups are below the plane of the paper, while the NH_2 and H groups are above the plane of the paper in case of serine molecule. Significant changes in the magnitudes of the geometrical parameters are observed as the basis set changes from 6-311++G** to aug-cc-pvdz at both level of calculations. The changes in bond lengths are more significant than the bond angles. All the bond lengths in case of serine are seen to elongate as we go from RHF level to B3LYP level. The bond lengths increases slightly as we increase the basis sets from 6-311++G** to aug-cc-pvdz. The bond angles of serine found at the B3LYP/6-311++G** and B3LYP/ aug-cc-pvdz levels are less than the corresponding bond angles found at the RHF/6-311++G** and

RHF/aug-cc-pvdz levels. Our calculated geometrical parameters agree satisfactorily with earlier reported experimental and theoretical results by Kistenmacher et al. and Friere et al. respectively [11, 12] for serine.

In case of threonine, all the bond lengths increases, except the CC bond length as the basis set changed from 6-311++G** to aug-cc-pvdz at both level of calculations (Table 2). The change in basis set does not change the CC bond lengths and it remains intact at both levels of theories. The bond angles of threonine found at the B3LYP/6-311++G** and B3LYP/ aug-cc-pvdz levels are slightly less than the corresponding bond angles found at the RHF/6-311++G** and RHF/aug-cc-pvdz levels. Table 3 shows the geometrical parameter of tyrosine molecule. The changes in geometrical parameters of tyrosine follow similar trends like serine and threonine.

The amino acids (H_2N-CHR-COOH) studied here only differ by their -R group, which contain a primary alcohol for serine, a secondary alcohol for threonine and a primary aromatic alcohol for tyrosine. Here, we may compare the bond lengths common to these three amino acids. The molecular structure of $–NH_2$ and COOH moiety are not considerably affected by the composition of –R group since the bond length and bond angles remains roughly constant whatever the amino acids studied. Only –N-CHR-C-group is readily affected by the nature of –R. The presence of the hydroxy group in the side chain of threonine leads a level of complexity not found in simple amino acids. Tyrosine is one of the three aromatic amino acids its side chain consists of a $–CH_2$ group bonded in Para position on a phenol ring. The theoretical calculations have revealed that the most stable form of tyrosine is one of the conformer in which the phenyl ring pointed towards the amino group on the other hand the less stable conformer has phenyl ring pointed towards the carbonyl group. Calculated geometrical parameters are compared with experimental values and with the results reported by earlier workers in Table 3. In Table 3 the geometric parameters calculated for tyrosine in gas phase are compared with calculated gas phase values. The significant change in bond lengths between the neutral and its zwitterionic form is only for CO bond at COOH moiety. This significant change is probably due to shifting of one hydrogen from the COOH group to the NH_2 group. This shift also influenced the bond angles in NH_3 and COO groups.

Total electronic energies of hydroxy amino acids (Serine, Threonine and Tyrosine) using RHF and B3LYP methods by employing 6-311++G** and aug-cc-pvdz basis sets with and without zero point energy corrections (ZPC) are listed in Table 4. The total electronic energy with ZPC and without ZPC at DFT/B3LYP level of theory with 6-311++G** and aug-cc-pvdz basis set are found to be minimum than the corresponding total electronic energy with ZPC at the RHF level of theory with corresponding basis sets. Further, if we go from lower basis set i.e 6-311++G** to higher basis set i.e aug-cc-pvdz yields a decrease in the total electronic energy. From Table 4 it is clear that threonine and tyrosine molecules follows similar trend like serine molecule.

Dipole Moments, Polarizabilities and Rotational Constants:

The calculated dipole moments, polarizabilities and rotational constants of hydroxy amino acids (serine, threonine and tyrosine) at the RHF and B3LYP level of theories with 6-311++G** and Aug-cc-pvdz basis sets in the gas phase are listed in Tables 5 and Table 6 respectively. Since there has been no experimental attempt to determine microwave spectra of gaseous threonine and tyrosine, the theoretically predicted rotational constants may be useful in searching gas phase conformers of serine, threonine and tyrosine with microwave spectroscopy. Similarly, theoretically predicted dipole moments may assists experimentalist on the permanent dipole measurement. At both level of the theories RHF and B3LYP when we go from lower basis set to higher basis set, the dipole moments slightly decreases in all the cases. This decrease is more at the B3LYP procedure which includes electron correlation than the RHF method. The dipole moments calculated at the B3LYP /6-311++G** level are in better agreement with the earlier results [1, 5, 12]. In fact the dipole moment calculated at the RHF/6-311++G** level agrees well with the dipole moment found earlier [12] for the serine. The polarizability tensor components also show a change in going from 6-311++G** basis set to Aug-cc-Pvdz basis set at both level of theories. The xx, xy, yy and zz components of serine and tyrosine increases while xz and yz component decreases at both level of theory by changing the basis set from lower level to higher level. In case of threonine xx, yy and zz component increases while xy, xz and yz component decreases. But they do not follow any regular pattern. The change in polarizability tensors xx, yy and zz are more pronounced in all cases considered here at both level of theory.

The rotational constant **A** and **C** of serine, threonine and tyrosine molecule decreases slightly, while Rotational constants **B** slightly increase when basis set changes from 6-311++G** to Aug-cc-Pvdz at both RHF and B3LYP level of theories.

Vibrational Characteristics:

Vibrational frequencies of hydroxy amino acids (serine threonine and tyrosine) obtained through the IR spectrum are analyzed with the help of calculated frequencies using ab initio and DFT calculations. The Infrared spectrums have been taken between 400 -4000cm^{-1} and are shown in Figure 4 for serine and Figure 5 for tyrosine respectively. There are fourteen (14), seventeen (17) and twenty four (24) atoms in the gaseous serine, threonine and tyrosine molecule respectively and these three molecules having 36, 45 and 66 vibrational modes respectively. But, the vibrational modes below 500 cm^{-1} are not listed in the tables for the sake of simplicity. The vibrational mode greater than 400cm^{-1} i.e thirty (30) vibrational modes for serine, thirty seven (37) vibrational modes for threonine and fifty five (45) vibrational modes for tyrosine are listed in the corresponding tables. Table 7-9 shows the observed and theoretically calculated vibrational frequencies at the RHF and DFT level of theory by employing 6-311++G** and aug-cc-pvdz basis sets for the hydroxy amino acids serine, threonine and tyrosine respectively. The vibrational assignments for corresponding vibrational frequencies are also included in these tables. As we know that scaling varies with method and basis sets, and different scaling factors 0.8929 in RHF [58] and 1.0167 in DFT [59] are recommended in the literature. Even with these scaling, the calculated frequencies do not match well with the observed ones for two reasons. One reason is of course that the calculations refer to gas phase where hydroxy amino acids are neutral while the observation refers to zwitterionic form of amino acids. Another reason may be the small differences between the calculated and the observed geometrical parameters. Therefore scaling has been not carried out, although there is a good agreement (within 100cm^{-1}) between observed and calculated frequencies. Also, the agreement is very well with other earlier reported vibrational frequencies for serine, threonine and tyrosine. The three different spectral regions of the infrared spectrum of these three hydroxy amino acids have been discussed below.

4000-2800 cm^{-1} region

We observed that magnitude of the calculated frequencies lying between 3900 cm^{-1} to 1500 cm^{-1} is decreased while for those below 1500 cm^{-1} there is an increase when we go from lower basis set to higher basis set and also from RHF to B3LYP level of calculation. Chakraborty et. al [60] have assigned calculated frequency at the RHF level of calculations for the zwitterion form of serine. The calculated vibrational frequencies at the DFT/B3LYP level of calculation of serine molecule are almost similar to the observed frequencies. The theoretically calculated frequencies at 3160, 3115 cm^{-1} were assigned as NH_3 stretch modes by other authors but from our calculation we obtained a frequency at 3123 cm^{-1} at DFT/B3LYP/aug-cc-pvdz level and have assigned it to CH_2 stretch. We have also compared the observed IR frequencies with unscaled calculated frequencies for neutral serine in Table 7. From this table, it is clear that magnitudes and the intensities of the calculated frequencies by different methods differ but follow a similar trend. From a study of IR spectrum of Glycine, Alanine, Serine, it is noted that frequencies above 1700 cm^{-1} to the limit of fundamental bands are not observed well except the peaks of CH stretching. A frequency range of 3700 cm^{-1} 2800 cm^{-1} in different methods are described by as usual and given in Table 7. Generally the ν (OH) for alcohol is assigned to have larger frequency than the ν (OH) for carboxylic acids but here in all cases reverse is true.

In case of threonine the O-H stretching of carboxylic acid group and O-H stretching of alcohol group have been found at the 3745, 3699 and 1798 cm^{-1} at the DFT/B3LYP/aug-cc-pvdz level of theory (Table 8). Our calculated stretching vibrational modes for O-H(carboxylic) and O-H(alcohol) are well agreed with earlier reported corresponding stretching vibrational modes by B.Lakard [31]. The stretching vibrational modes for NH_2, CH_3, CH, CN are also in a good agreement with earlier reported corresponding stretching vibrational modes [31,33]. The NH_3 stretching vibrations present in all amino acids. The NH_3 molecule has C_{3v} symmetry while the symmetry of amino group in crystal threonine is C_1. The asymmetric stretching of NH_3 was observed at 3026 and 3169 cm^{-1} by Silva et al [33], our calculated stretching modes of NH_3 has been found at 3602 and 3503 cm^{-1} are higher than the observed ones by Silva et al but well agreed with theoretically calculated by B.Lakard [31]. The CH vibration modes has been found from 3121cm^{-1} to 3004 cm^{-1} at DFT/B3LYP/aug-cc-pvdz level of theory and in good agreement with observed ones 2882 cm^{-1} and 2932 cm^{-1} by Silva et al as C-H stretching modes.

The stretching vibrational modes have been found at the 3736, 3816 and 1794 cm^{-1} for the corresponding O-H stretching of carboxylic acid group and O-H stretching of alcohol group at the DFT/B3LYP/aug-cc-pvdz level of theory and well agreed with earlier reported theoretical calculation (Table 9) at the CASSCF level of theory by Samuels et al.[43] of tyrosine molecule. In the observed IR spectrum in liquid and solid phase stretching vibrational modes have been predicted at the 3930 cm^{-1} for O-H of COOH and 4048 cm^{-1} O-H for alcohol. The theoretically calculated stretching modes for both O-H groups agree well with observed ones. The asymmetrical NH_3 stretching vibrational mode has been found at the 3564 and 3573 cm^{-1} at the B3LYP/aug-cc-pvdz and B3LYP/6-311++G** basis set. The Ramaekers et al [38] reported this asymmetrical NH_3 stretching vibrational mode at 3408 cm-1. The symmetrical NH_3 stretching vibrational mode is almost 100cm^{-1} lower than the asymmetrical stretching vibrational modes. The CH stretching vibrational modes may be divided into two groups, first is the aromatic C-H and second is aliphatic C-H stretching vibrational modes. The former C-H stretching vibrational modes found above the 3000 cm^{-1} and latter being below the 3000 cm^{-1}. The theoretically calculated values are in good agreement with observed ones.

2000-1000 cm^{-1} region

Chakraborty [60] et al have observed a band ascribed to ν C=O stretch at 1734 cm^{-1} but in our IR measurements, this band is observed at 1658 cm^{-1} and 1635 cm^{-1} in liquid and solid phase respectively but theoretical analysis predict a band near 1997,1982 cm^{-1} at the RHF level and 1809 and 1799 cm^{-1} at the DFT/B3LYP level with 6-311++G** and aug-cc-pvdz basis set correspondingly for C=O stretching in serine. For lower frequencies the agreement between our calculated values and those earlier reported is better. A frequency at 1504cm^{-1} observed in the IR spectrum may be assigned to CH_2 scissoring. The two bands at 1433cm^{-1}, 1352 cm^{-1} are assigned to involve mixing of CH bend and NH bending modes. Pawlukojc et al [61] have assigned the CH_2 rocking vibration at 1353cm^{-1} and 1320 cm^{-1} in the IINS spectrum of L-serine while our calculation indicate that these vibrations be attributed to a mixing of CH_2 bend, NH_2 bend and COH bend. Although our experimental observations are limited to 400 cm^{-1} theoretical calculation permits us to predict the frequencies below 400 cm^{-1} which are due to torsion of different group.

In threonine, the theoretically calculated C=O stretching vibrational mode at the DFT/B3LYP level of theory with 6-311++G** and aug-cc-pvdz is found at the 1798 and 1807 cm^{-1} respectively and well agreed with C=O stretching mode reported by B.Lakard [31] (Table 8). The bending mode of the CH_3 has been found at the 1466 and 1476 cm^{-1} at the DFT/B3LYP level of theory with aug-cc-pvdz. Basis set. Bending vibrational mode of CH group has been found in between 1385 $cm^{-1}$to 1215 cm^{-1}.

The most prominent band observed in the 2000-1000 cm^{-1} region is C=O stretching vibrational mode in tyrosine. In liquid phase this bands originate at 1701 cm^{-1} while in solid phase at 1902 cm^{-1}. The theoretically calculated C=O stretching vibrational mode is found at the 1794 and 1803cm^{-1} with 6-311++G** and aug-cc-pvdz respectively at the DFT/B3LYP level of theory. The calculated and observed C=O stretching vibrational mode is well agreed with earlier reported results [38, 43]. The C-C stretching vibrational mode originates at around 1500 cm^{-1}, while C-H stretching mode originates in between 1500-1000cm^{-1}. The bending vibrational mode of O-H group of COOH has been found at 1253 cm^{-1} at DFT/B3LYP level of theory, whereas the vibrational mode of O-H group of alcohol has been found at 1155 cm^{-1}.

1000-400 cm^{-1} region

The lower region of the IR spectrum of serine, threonine and tyrosine molecules is complex in nature. The vibrational bands originates in this region are basically due to deformation in the skeleton of the molecule, deformation in the different functional groups, torsions in the different groups and mixing of different type of motions in the molecule.

Conclusion:

The molecular structures of serine, threonine and tyrosine molecules in its neutral form have been optimized using ab initio quantum mechanical calculations and DFT level of theory. We have determined the molecular structures, Dipole moments, Polarizabilities, Rotational constants and Vibrational frequencies of these selected three hydroxy amino acids. It is clear that the geometrical parameters obtained for these three amino acids are basis sets dependent. The addition of polarization function leads to longer bond length and shorter bond angles. The changes in different stretching vibrational modes of O-H groups have been analyzed from serine to tyrosine.

Table 4: Total electronic energies of Serine, Threonine and Tyrosine using RHF and B3LYP methods by employing 6- 311++G and aug-cc-pvdz basis sets without and with zero point energy corrections. All energies are given in atomic unit (a.u.).**

Methods/ Basis Set		Serine		Threonine		tyrosine	
		Without ZPC	With ZPC	Without ZPC	With ZPC	Without ZPC	With ZPC
RHF	6-311++G**	-396.849717	-396.727237	-435.897448	-435.745532	-626.445840	-626.238621
	Aug-cc-pvdz	-396.796341	-396.674213	-435.838784	-435.687258	-626.368249	-626.161247
B3LYP	6-311++G**	-399.096551	-398.983240	-438.425267	-438.284285	-630.207668	-630.014870
	Aug-cc-pvdz	-399.030951	-398.918111	-438.350257	-438.211864	-630.111793	-629.919145

Table 5: Dipole moment (Debye) and Polarizabilities of Serine, Threonine and Tyrosine using RHF and B3LYP methods by employing 6-311++G and aug-cc-pvdz basis sets.**

Molecules	Dip./ Pol.	Method/Basis sets			
		RHF		B3LYP	
		6-311++G**	Aug-cc-pvdz	6-311++G**	Aug-cc-pvdz
Serine	μ	3.0582	2.9439	3.0050	2.8772
	α_{xx}	51.097	54.620	59.932	63.594
	α_{xy}	0.562	0.738	0.976	1.190
	α_{yy}	51.333	54.376	59.510	62.609
	α_{xz}	-3.215	-2.792	-3.335	-2.981
	α_{yz}	3.389	2.881	3.273	2.807
	α_{zz}	46.160	48.796	52.308	55.118
Threonine	μ	3.0626	2.9576	3.0190	2.9138
	α_{xx}	66.348	70.361	77.282	81.368
	α_{xy}	1.019	0.538	0.855	0.367
	α_{yy}	60.826	63.770	69.905	72.896
	α_{xz}	3.354	3.090	3.542	3.370
	α_{yz}	2.738	2.416	2.420	2.150
	α_{zz}	54.314	57.251	61.074	64.213
Tyrosine	μ	0.3878	0.2693	0.5796	0.3960
	α_{xx}	145.631	152.802	169.309	176.584
	α_{xy}	0.212	0.971	1.587	2.569
	α_{yy}	114.238	118.874	125.986	130.551
	α_{xz}	-8.083	7.923	-9.719	9.436
	α_{yz}	4.701	-4.697	4.014	-4.529
	α_{zz}	77.972	82.937	82.948	88.254

Table 6: Rotational constants of Serine, Threonine and Tyrosine using RHF and B3LYP methods by employing 6-311++G and aug-cc-pvdz basis sets.**

Molecules	Rot. Const.	RHF		B3LYP	
		6-311++G**	Aug-cc-pvdz	6-311++G**	Aug-cc-pvdz
Seri ne					
	A	3.57757	3.55912	3.56991	3.55602
	B	2.31999	2.32069	2.24077	2.23961
	C	1.79767	1.79036	1.75647	1.74815
Threonine	A	3.20027	3.19212	3.12809	3.12083
	B	1.51074	1.50992	1.47628	1.47373
	C	1.31433	1.30953	1.29498	1.29169
Tyrosine	A	2.32658	2.32260	2.27362	2.27376
	B	0.34455	0.34323	0.34190	0.34036
	C	0.31435	0.31386	0.31098	0.31089

Table 7: Calculated and experimental fundamental frequencies (cm^{-1}) of Serine

No.	Calculated frequencies				Exptal.[a] (IR)		Assignments
	RHF		B3LYP		In nujoll mull (liquid)	KBr (Solid)	
	6-311++G**	Aug-cc-pvdz	6-311++G**	Aug-cc-pvdz			
1	513 (92)	506 (108)	481.2(33)	479.5(34)	499	500	δ O8H9
2	545 (66)	538.2(46)	527.6(27)	524.8(22)	524	525	δ O8H9
3	562.3 (70)	556.5(53)	568.4(56)	552.3(70)	567	563	δ O13H14
4	642.2(70)	636.8(62)	601.7(119)	592.4(81)			δ O13H14
5	678.3(83)	673.8(77)	639.1(80)	637.1(73)	619	618	δ O8H9
6	821.5(44)	818.5(41)	753.5(33)	750.3(33)	727	728	T C2C4
7	895.9(103)	894.1(87)	816.7(63)	813.8(54)	814	816	W NH2
8	978.5(44)	980.8(32)	883.7(92)	882.3(79)	850	848	,,
9	987.3(49)	985 (55)	910.7(25)	910.7(21)	898	900	T C2C3+ W NH2
10	1082.6(1)	1077.5(0.3)	1000.4(2)	994.4(1)	981	980	δ_{as} C3H5-C3H6 +δ_{as} C2H12-N1H11
11	1187 (85)	1181.3(83)	1074.5(88)	1074.5(82)	1028	1030	υ C3O13
12	1232 (53)	1229.2(48)	1117.2(84)	1119.7(74)	1093	1094	υ N1C2
13	1278.1(173)	1273.3(151)	1157.1(174)	1156.4(159)	1149	1152	δ O8H9, δ C2H12, T_w NH2
14	1324 (41)	1320.7(51)	1214.9(45)	1206.3(56)	1180	1182	,,
15	1333.3(117)	1328.6(118)	1222.5(22)	1216.6(21)			δ C2H12
16	1433.1(15)	1431.5(8)	1295.2(3)	1290.9(4)	1246	1247	δ C2H12
17	1452 (32)	1447.9(25)	1324.3(25)	1321.4(19)	1311	1312	δ O8H9 + δ C2H12
18	1491.1(8)	1480.4(7)	1368.8(4)	1353.9(4)	1352	1353	δ C2H12 +δ C3H6+δO13H14
19	1553.5(49)	1546.2(57)	1420.5(27)	1414.2(40)	1433	1432	δ C3H5+δ O13H14
20	1577.5(41)	1570.2(37)	1433.1(43)	1423.9(38)	1504	1509	δ O13H14+WC3H5H6
21	1638.1(3)	1620.2(3)	1509 (3)	1489.1(3)	1580	1583	ScC3H5H6
22	1781.5(65)	1762.1(61)	1637.4(70)	1615.5(63)			Sc N1H10H11
23	1997.1(427)	1982.6(395)	1809.3(303)	1799.9(283)	1658	1635	υC4O7
24	3138.3(28)	3141.3(29)	2975.8(35)	2981.5(26)			υC3H6 + υ C2H12
25	3159 (86)	3165.9(86)	2988.7(68)	2995.2(77)	3011		υC2H12+ υ C3H6
26	3273.3(26)	3280 (26)	3114.1(15)	3123.8(15)			υC3H5
27	3756.1(11)	3748.6(9)	3517 (13)	3503.6(11)			υ_s N1H10H11
28	3841.6(25)	3838.9(23)	3607.4(22)	3598.8(21)	3600		υ_{as} N1H10H11
29	4118.1(144)	4112 (133)	3727.9(62)	3713.8(55)	3700		υO13H14
30	4133.4(76)	4126.7(68)	3762.5(83)	3745.4(78)	3755	3754	υO8H9 of COOH

Vibrational spectra recorded in a nujoll mull. Numbers shown in the parenthesis correspond to the IR intensities. υ=Stretching, υ_{as}=Asymmetric stretching, υ_s=Stretching, δ=bending, δ_s= Symmetric bending, δ_{as}= Asymmetric bending, T=torsion, W = wagging, Sc= scissoring, T_w = twisting and Φ=deformation in molecule

Table 8: Calculated and experimental fundamental frequencies (cm^{-1}) of Threonine

S. No.	Calculated frequencies				Expt [a] (IR)	Ref.[b]	Ref.[c]	Assignments
	RHF		B3LYP					
	6-311++G**	Aug-cc-pvdz	6-311++G**	Aug-cc-pvdz				
1	485.5(3)	482.8(2)	450.3(4)	448(4)	447			Φ
2	511.9(69)	504.8(98)	475.7(28)	473.5(29)	491			Φ
3	540.3(97)	531(61)	545.6(22)	539(32)				T_w of OH
4	583.7(109)	579.4(88)	574.7(164)	558(129)	560			Φ
5	678.5(68)	672.8(65)	630(58)	625(53)				Φ
6	705.1(31)	700.4(29)	659.2(34)	654.4(32)				Φ
7	794.6(46)	792(42)	728(28)	725(27)	747			Φ
8	909.8(94)	908.2(75)	830(76)	828(61)				WNH_2
9	946.5(11)	946.6(12)	869(24)	870.3(25)	871			δ NH_2
10	981.9(80)	982(75)	892.4(77)	890.3(65)				Φ
11	1022.4(1)	1020.4(1)	937.4(.7)	937.7(.8)	932			Φ
12	1110.9(22)	1105.3(20)	1026.3(25)	1020.1(21)				δ CH_3
13	1184.3(26)	1186(42)	1076.2(53)	1079.3(55)	1040		1071	T_w CC
14	1192.2(59)	1187(43)	1104.3(27)	1098.7(23)	1093			T_w CC
15	1265.8(131)	1262(120)	1135.8(154)	1136.3(133)				υ CC
16	1284.2(120)	1280.6(102)	1162.5(113)	1160.6(110)	1185		1165	T_w CH
17	1337.2(122)	1332.1(134)	1221.1(49)	1215.6(59)				T_w NH_2
18	1379.6(17)	1378.2(17)	1257.6(21)	1251(18)	1246			Φ
19	1423(11)	1419.6(5)	1301.6(3)	1293.9(1)			1253	T_w CN
20	1468(24)	1461(16)	1336.8(24)	1328.5(19)	1318			δCH
21	1495.3(13)	1486.1(10)	1369.5(11)	1358.3(10)	1347		1354	δCH
22	1531.1(9)	1519.3(10)	1401(5)	1385(8)	1383			W CH_3
23	1558.4(56)	1546.5(60)	1415.9(23)	1410.7(25)				Φ + δ CC
24	1567.9(43)	1562.1(41)	1430.8(55)	1416.5(59)	1418		1402	δCH
25	1607.9(8)	1590.8(10)	1489(6)	1466.1(6)	1457			δCH_3
26	1620.9(2)	1601.3(2)	1501.1(5)	1476(5)			1478	δCH_3
27	1785.8(73)	1767.8(69)	1641.7(77)	1623.6(69)	1626		1656	W NH_2
28	1994.4(429)	1979.8(396)	1807.7(304)	1798.2(282)	1651		1804	υ C=O of COOH
29	3152.7(19)	3154(22)	2999.8(20)	3004.7(20)	2873			υ_s C-H
30	3163.1(32)	3167.7(30)	3022.9(23)	3028.1(23)	2978	2974		υ_s C-H of CH_3
31	3221.6(23)	3232.1(20)	3078.3(2)	3090(1)	2998	2912	2840	υ_s C-H
32	3240.2(25)	3250.8(26)	3094.8(35)	3106(36)		2989	2862	υ_s C-H_2
33	3258.7(46)	3266(49)	3109.1(23)	3121.7(23)			2914	υ_{as} C-H_2
34	3760.9(15)	3754.1(13)	3516(19)	3503.3(17)	3026	3353	3397	υ_s N-H_2
35	3845.7(26)	3843.2(24)	3611.6(22)	3602.5(21)	3169	3505	3469	υ_{as} N-H_2
36	4117.7(148)	4112(138)	3712.8(61)	3699.2(55)		3600	3758	υ O_{16}-H_{17}
37	4123.2(68)	4117.2(62)	3762(84)	3745(79)		3686	3705	υ O_6-H_7 of COOH

[a] [Reference 33], [b] [Reference 31], [c] [Reference 32]

Vibrational spectra recorded in a nujoll mull. Numbers shown in the parenthesis correspond to the IR intensities. υ=Stretching, υ_{as}=Asymmetric stretching, υ_s=Stretching, δ=bending, δ_s= Symmetric bending, δ_{as}= Asymmetric bending, W = wagging, Sc= scissoring, T_w = twisting T=torsion, Φ=deformation in molecule

Table 9: Calculated and experimental fundamental frequencies (cm^{-1}) of Tyrosine

S. No.	Calculated frequencies				Exptal.[a] (IR)		Ref.[a]	Assignments
	RHF		B3LYP		In nujoll mull (liquid)	KBr (Solid)		
	6-311++G**	Aug-cc-pvdz	6-311++G**	Aug-cc-pvdz				
1	545(11)	542.8(11)	500.3(10)	500.7(10)	500	491	571	δ C-C
2	599.3(9)	598(10)	550.2(18)	550.7(18)	550	528	600	δ C_{18}-C_{20}
3	623.6(160)	623.2(143)	597.2(125)	600.5(111)	600	575	680	δ C-C-N
4	701.4(.6)	699.4(0.7)	653.5(6)	648(7)			712	δ C-C ring
5	717.6(15)	712(14)	657.3(3)	652.4(1)			755	δ C-C ring
6	767.3(12)	766(10)	709.6(12)	710.8(11)	680	648	761	δ O_{22}-H_{24}
7	806.1(4)	806.7(4)	738.4(5)	745(4)	750	712	809	υ C-COOH
8	907.6(18)	903.6(20)	812.3(16)	812.8(8)	800	798	851	δ N-H
9	927.1(75)	924.2(67)	843.9(43)	844.4(35)	860	840	883	δ C-H ring
10	942.7(84)	943.5(70)	863.9(74)	864.9(64)	877	877	898	δ C-H ring
11	955.7(12)	952.6(15)	879.6(.7)	878(0.3)	896		920	δ C_9-C_5
12	1061.4(2)	1054.6(4)	952.2(10)	954.4(8)	939	940	1035	δ C-H ring
13	1081.5(38)	1078.3(7)	967.1(1)	968.7(1)			1041	υ C_3-C_5
14	1087(3)	1081.2(39)	989.9(15)	987.6(15)	983	984	1078	δ C-H
15	1103.4(2)	1100(2)	1030.5(1)	1023.8(1)	1041	1041	1120	δ C-C
16	1171.1(29)	1176(22)	1114.2(27)	1110.2(6)	1099	1100	1181	υ C_3-N_1
17	1199.3(20)	1196.1(18)	1122.4(152)	1123.2(163)			1206	δ OH-CH
18	1229.2(51)	1229.8(49)	1146.1(123)	1144.9(52)	1111		1220	δ C-C ring
19	1264.4(122)	1262.5(127)	1159.5(31)	1152.8(83)	1155	1157	1260	δ O_{20}-H_{21}
20	1283.6(60)	1276.1(51)	1188.2(157)	1186.8(99)			1301	δ C-H ring
21	1312.3(2)	1312.7(2)	1227.1(0.9)	1225.1(2)	1215		1326	υ C-C
22	1351(80)	1353.4(72)	1263.5(9)	1253.6(17)	1244	1244	1338	δ O-H of COOH
23	1382.7(86)	1376.8(80)	1276.2(116)	1273.9(105)			1374	υ C_{18}-O_{20}
24	1385.3(68)	1379.1(69)	1297.6(2)	1291.7(2)			1367	δ C-H
25	1424.4(11)	1418.5(11)	1332.4(30)	1330(22)			1431	υ C_5-O_{22}
26	1472.6(19)	1464(20)	1359.4(8)	1348.3(14)	1331	1330	1490	δ C-H
27	1506.2(15)	1497.4(17)	1361.8(17)	1369.5(17)	1363	1364	1511	δ C_3-H
28	1556.7(19)	1546.3(22)	1420.3(5)	1406.8(8)			1526	δ CH_2
29	1583.4(22)	1580.4(24)	1466.8(19)	1462.9(14)	1415	1416	1579	υ C-C
30	1614(5)	1595.3(5)	1488.8(8)	1469.1(12)	1452	1453	1655	δ CH_2
31	1676.6(138)	1672(135)	1543.8(112)	1538.8(111)	1512	1514	1681	υ C-C ring
32	1775(20)	1780.3(22)	1631.4(15)	1636.6(17)			1734	υ C-C ring
33	1804(61)	1794(26)	1653.6(50)	1652.7(27)	1587	1589	1774	υ C-C ring
34	1809.6(35)	1806.4(58)	1670.8(32)	1657.8(44)	1612		1852	υ C-C ring + δ NH_2
35	1990.3(460)	1976.1(423)	1803.3(342)	1794.4(315)	1701	1902	1960	υ C=O
36	3180.2(24)	3186.7(24)	3031.6(19)	3040.6(19)			3191	υ CH_2 +CH ring
37	3223(8)	3230.1(8)	3069(7)	3079.9(7)			3229	υ CH_2 +CH ring
38	3235.2(23)	3243.8(24)	3084(15)	3096.7(15)		2958	3248	υ CH_2
39	3306.8(25)	3317(24)	3148.7(22)	3159.4(22)			3344	$υ_{as}$ C-H ring
40	3350.2(16)	3357.2(15)	3191.8(9)	3198.3(12)			3368	$υ_s$ C-H ring
41	3352.4(1)	3360(2)	3195(2)	3200.2(0.6)	3206	3208	3399	$υ_s$ C-H ring
42	3735.7(7)	3727.8(6)	3495.5(4)	3481.8(3)			3775	$υ_s$ NH_2
43	3812.5(10)	3807.4(9)	3573.8(8)	3564(7)			3887	$υ_{as}$ NH_2
44	4112.5(141)	4106.6(132)	3748(67)	3731.8(63)			3930	$υ_s$ O-H of COOH
45	4189.1(107)	4181.2(103)	3836.2(68)	3816.5(66)			4048	$υ_s$ O-H

[a] [Reference 43]

Vibrational spectra recorded in a nujoll mull. Numbers shown in the parenthesis correspond to the IR intensities. υ=Stretching, $υ_{as}$=Asymmetric stretching, $υ_s$=Stretching, δ=bending, $δ_s$= Symmetric bending, $δ_{as}$= Asymmetric bending, W = wagging, Sc= scissoring, T_w = twisting T=torsion, Φ = deformation in molecule

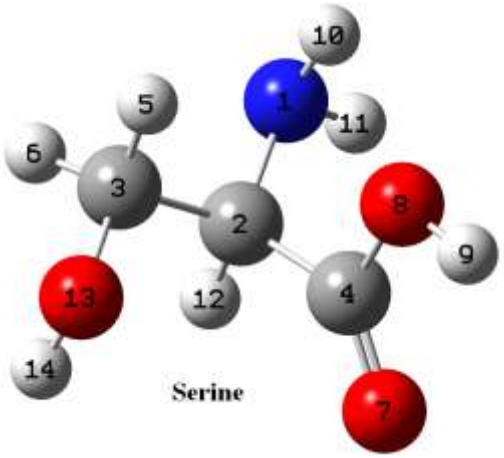


Figure 1: Molecular structure of Serine obtained at the DFT/B3LYP/Aug-cc-Pvdz level of theory.

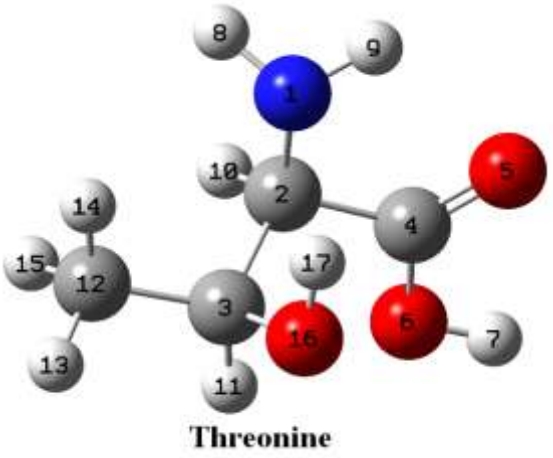


Figure 2: Molecular structure of Threonine obtained at the DFT/B3LYP/Aug-cc-Pvdz level of theory.

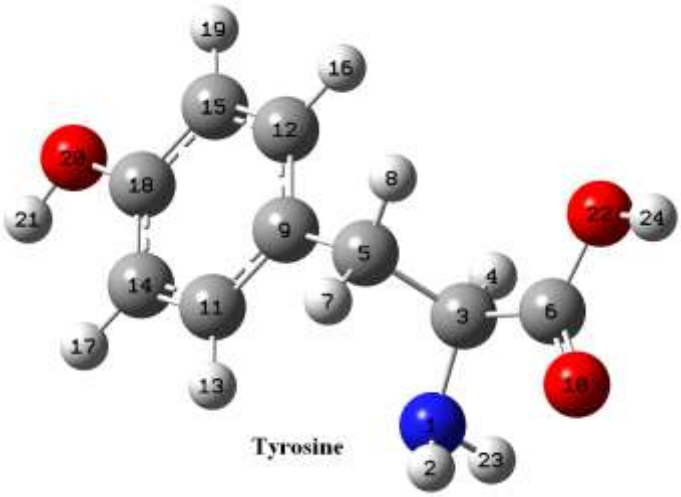
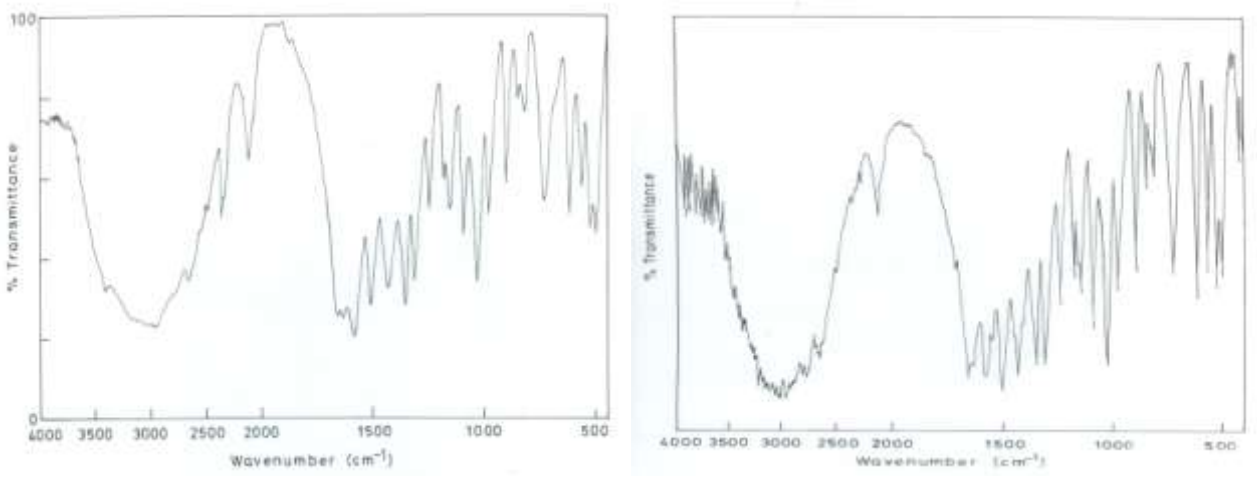
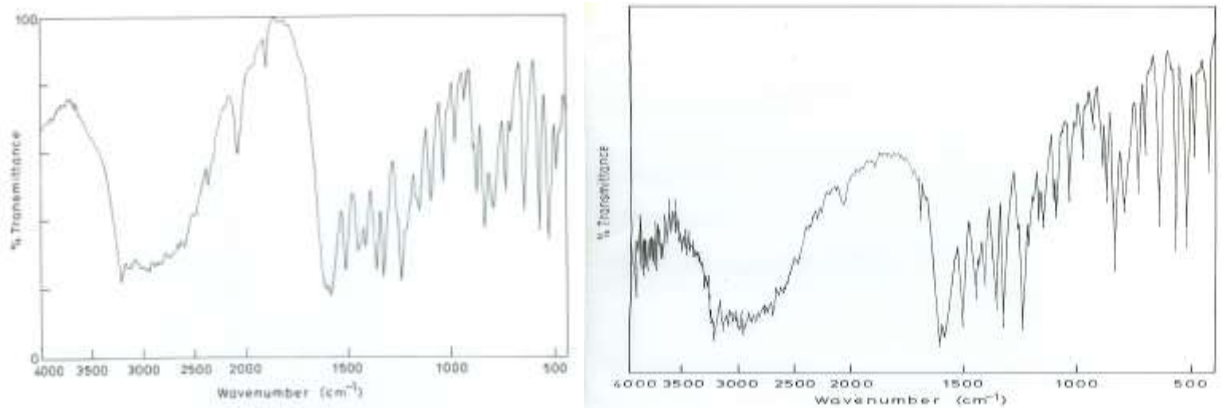


Figure 3: Molecular structure of Tyrosine Molecule obtained at the DFT/B3LYP/Aug-cc-Pvdz level of theory.



(a) **(b)**

Figure 4: IR spectrum of serine molecule



(a) **(b)**

Figure 5: IR spectrum of tyrosine molecule

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