



## Vibrational Spectroscopy

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### Spectroscopic studies of L-Cysteine: DFT calculations

Santosh Kumar<sup>1,\*</sup>, Amareshwar K. Rai<sup>2</sup>, S. B. Rai<sup>3</sup> and D. K. Rai<sup>4</sup>

<sup>1</sup> DAV Institute of Engineering & Technology, Daltonganj, Jharkhand, India.

<sup>2</sup> Ozone Unit Department of Geophysics, BHU, Varanasi..

<sup>3</sup> Laser and Spectroscopy Laboratory, Department of Physics, BHU, Varanasi, India.

<sup>4</sup> Laser and Spectroscopy Laboratory Department of Physics, BHU, Varanasi, India.

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#### ABSTRACT

The infrared and Raman spectra of L-cysteine molecule has been recorded in the nujol mull as well as in the aqueous solution in the range of 4000-400cm<sup>-1</sup>. The observed infrared and Raman frequencies are assigned on the basis of the theoretically calculated vibrational frequencies for the most stable structure of zwitterionic cysteine hydrated with six water molecules at B3LYP/6-311G\* level. The electronic absorption spectrum of the cysteine molecule has been measured in solution at different concentrations and at different pH in the range of 400- 200 nm. It is observed that the electronic absorption band shifts with the change of pH as well as the concentrations. The TDDFT calculations for the same molecule (zwitterionic cysteine + six water molecules) has also been carried out at B3LYP/6-311G\* level. The optimized bond lengths and bond angles for the most stable structure of cysteine hydrated with six water molecules were compared with those reported for X-ray data for cysteine.

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#### 1. Introduction

The spectroscopic and the structural aspects of L-Cysteine molecule have been investigated theoretically as well as experimentally by several workers [1-6]. The basic difference between this amino acid and the others is that it contains a thiol group. It also exists in several isomeric forms in crystalline state, in solution and in gas phases. These different isomeric forms serve as the models for the investigations of a wide range of intermolecular interactions that have importance in chemistry and in biology [7]. These include proton transfer, which is central to the catalysis and to many biochemical processes. The low frequency vibrations give the information for the weak interactions taking place in the enzyme reactions, self-assembly of super molecule and the intermolecular interactions [8]. Two polymorphic phases orthorhombic (P 2<sub>1</sub> 2<sub>1</sub> 2<sub>1</sub>, Z=1) and a monoclinic (P 2<sub>1</sub>, Z=2) of L- cysteine are known and referred to as the L-Cysteine-I and L-Cysteine-II respectively. Their crystal structure have been studied by X- ray diffraction [9, 10] at 120K which shows that two symmetric and independent molecules in the asymmetric unit cell denoted by L-cysteine (A) and L-cysteine (B). These two conformations are corresponding to the zwitterionic cysteine as shown in Fig.1. Sulfhydryl group of cysteine molecule is important in structural biochemistry. In the proteins, the thiol group has the property to form hydrogen bonds with solvent molecules as well as with other protein groups. The study of the molecular structure and the vibrational spectrum of the amino acids provide valuable information about the molecular configuration and nature of the hydrogen bonding in these systems. Edsall et al. [11] have interpreted the vibrational Raman spectra of several amino acids including the cysteine molecule. Such vibrational spectra are useful in the identification of the polarization of the donor covalent bond (S<sup>-d</sup>

H<sup>+d</sup>) in the presence of an acceptor group. Several authors have noted the sensitivity of aliphatic and S-H bond of the cysteine to the different solvents and crystal lattice environments [12-16]. Huimin et al. [17] have studied the structure of viruses using Raman technique and have shown that the S-H stretching frequency of the viral coat proteins may significantly vary from one virus to another. They have also shown that this sulfhydryl group is highly sensitive to the deuterium exchange and to change in the pH, ionic strength and several other factors which control virus assembly [18-22]. Huimin et al. [23] have also reported the Raman spectra of normal and deuterated cysteine compounds and performed normal coordinate calculations. Schafer et al. [24] have studied the conformation and the structure of cysteine while Gronert et al. [25] have carried out ab initio studies on several amino acid conformations. Chakraborty et al. [26] have studied the ground state vibrational spectra of cysteine assisted with theoretical calculations. A neutron diffraction study of L-cysteine has also been made to determine its structure [27]. The thiol group in the cysteine residue side chain is responsible for the stabilization of the secondary structure of the proteins and hence it is the subject of a number of spectroscopic studies for characterizing its conformers [28]. The full conformational search of this molecule has been carried out in the gas as well as in the solution phases by Dobrowloski et al. [29]. The results indicate that the zwitterionic structure of the cysteine molecule is most stable in the solution that is quite similar to the structure obtained in the crystalline state. The stability of the conformers of the solvated structure is based on either relative electronic energy or relative free energy obtained in solution using the solvation model of Gaussian program. However, this model does not include the short range interaction between the solute

Tele:

E-mail addresses: [bhu.santosh71@gmail.com](mailto:bhu.santosh71@gmail.com)

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molecule and the water molecules of the solvent. Thus, this may lead to uncertainty for the most stable structure of the molecule. The inclusion of the explicit water molecule around the polar sites of the solute molecule may overcome this difficulty. This can be easily done using the super molecular approach combined with solvation model. In the super molecular approach, explicit water molecules are added around the polar sites of the solute molecule. Bachrach et al. [30] have studied the microsolvation of cysteine molecule at PBE1PBE/6-311+G (d,p) level. According to this calculation, zwitterionic structure of cysteine is isoenergetic with neutral structure of cysteine molecule with six explicit water molecules in gas phase. Vibrational spectrum of the zwitterionic cysteine molecule with three explicit water molecules has also been studied by Tiwari et al. [31]. But results indicate that the canonical structure of the cysteine molecule is still more stable than its zwitterionic structure in gas phase. Therefore, the reported infrared spectra at ab initio level lack either of consideration of electron correlation in their method or in terms of sufficient number of explicit water molecules around the polar sites of the solute molecule.

Figure 1

The structure of the zwitterionic cysteine

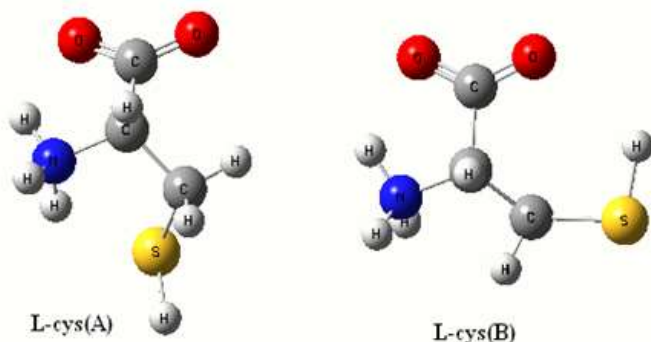
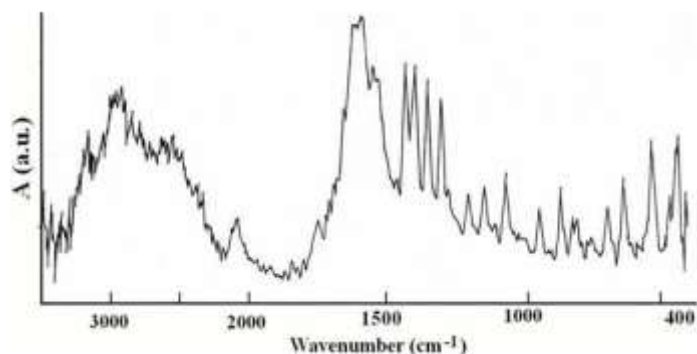


Figure 2

Infrared spectrum of cysteine molecule in solid form



So, the observed infrared and Raman spectra of cysteine molecule needs to be reinvestigated. We therefore, calculated the vibrational frequencies of the most stable zwitterionic structure of cysteine with six water molecules as reported by Bachrach et al. [30], The calculated vibrational frequencies of the zwitterionic cysteine with six water molecules are compared with our observed infrared and Raman frequencies. We have also measured the electronic absorption spectrum of the cysteine molecule at different concentrations and at the different pH. The observed absorption is compared with theoretically calculated electronic excitation energies at TDDFT at B3LYP/6-311G\* level.

## 2. Experimental Method

L-cysteine sample obtained from Merck (99% purity) has been used to record the infrared (I.R.) and the Raman spectra. The IR spectrum of cysteine has been recorded in nujol mull as well as in water using a Fourier Transform Infrared spectrophotometer (JASCO FTIR-5300) in the range of 400-4000  $\text{cm}^{-1}$ . For IR spectrum in solution, repeated scans has been made to get appreciable intensity of the bands. The Raman spectrum was recorded using an ISA Jobin -Yvon Spex HR- 320, f/4 monochromator (600g/mm grating). The excitation laser is a SDL- 8430 diode laser with pump wavelength of 785 nm with 140 mw output power. Here again, repeated scans has been taken. The IR spectra of cysteine molecule in solid and in solution form are shown in Fig.2 and Fig.3 respectively whereas the Raman spectra in solid form is given in Fig.4. For electronic absorption spectrum a Systronic-117 model UV-VIS-NIR-Spectrophotometer has been used. We have also recorded the electronic spectrum of cysteine at different concentrations as well as at different pH as shown in Fig. 5.

Figure 3

Infrared spectrum of cysteine molecule in solution

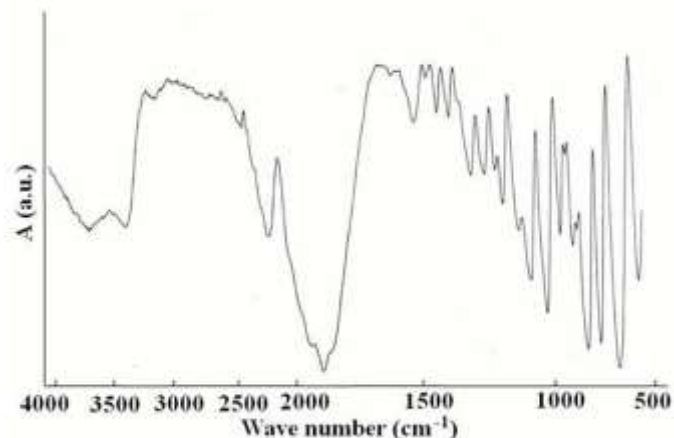
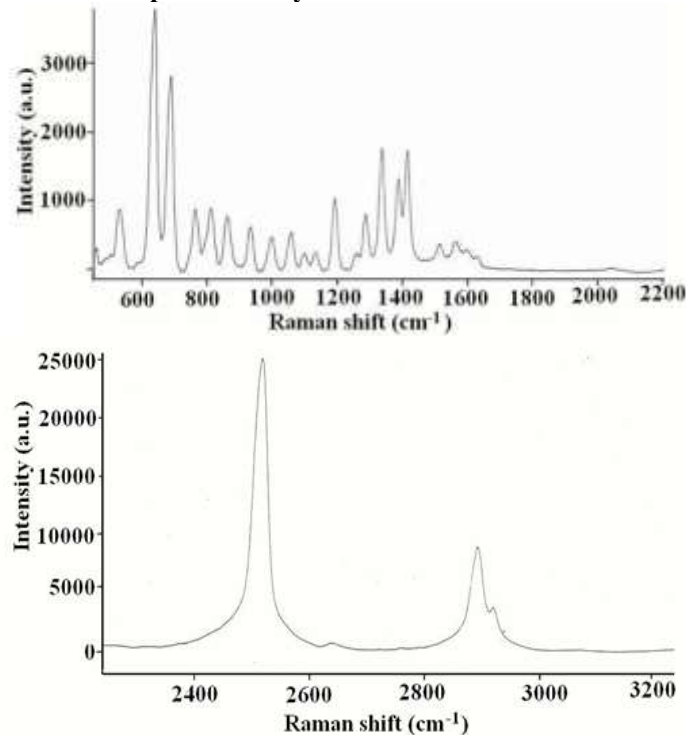


Figure 4

Raman spectrum of cysteine molecule in solid form



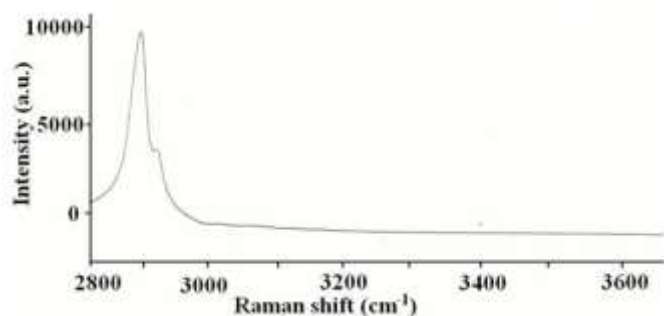


Figure 5

### Electronic absorption spectrum of cysteine molecule in solution

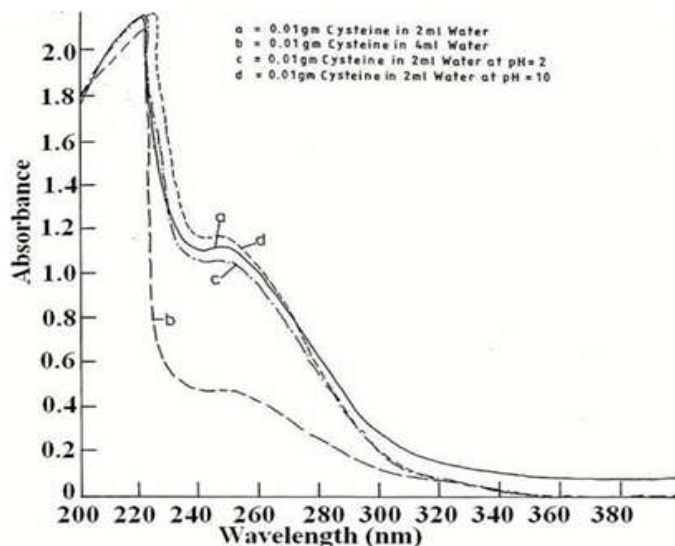
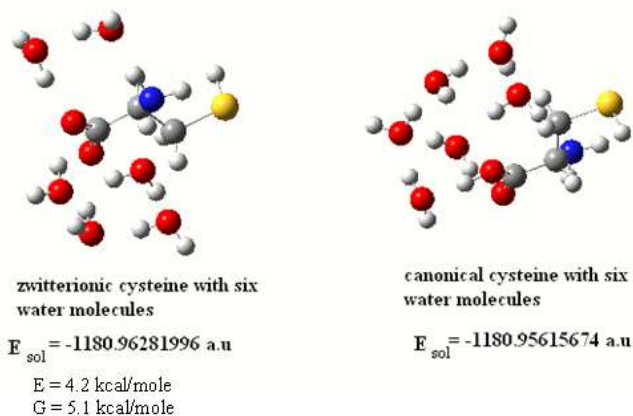


Figure 6

### The most stable structure of zwitterionic cysteine with six water molecules



(E and G are the differences in the electronic energies and free energies of above mentioned structure in solution)

### 3. Computational details

All calculations have been carried out using the Gaussian 03W program package [32]. Since the HF approximation is not reliable enough for quantitative predictions in conformational analysis while DFT and Moller Plesset theory with medium sized basis sets including diffuse functions ought to be used to get reasonable results as these include electron correlations also. We have used DFT/B3LYP method for characterization of the vibrational spectrum of the cysteine molecule. Because, it involves a small computer time as compared to MP2 calculations. Also, a better correlation between theoretical and

the observed vibrational frequencies in several other amino acids was found as can be seen in the references [33-40]. Though, there are several hydrated conformers of the canonical cysteine and its zwitterionic structures possible up to six water molecules, we have not considered the structures of cysteine (canonical & zwitterion) hydrated with one, two, three, four and five water molecules as these structures do not show considerable energy difference between the zwitterionic cysteine and its counterpart (canonical cysteine) as can be seen in reference [30]. Therefore, we have taken the geometry of the most stable structure of both, the canonical and the zwitterionic cysteine hydrated with six water molecules. This structure is again optimized at B3LYP/6-311G\* level in gas phase. All real frequencies show the true minima. The scaling factor of 0.96 is used for all calculated vibrational frequencies as recommended by Scott and Radom [41]. Further, the single point energy calculations have been carried out in the solution using the CPCM model at B3LYP/6-311++G\*\* level. The vertical electronic excitation energies for the most stable structure of the zwitterionic cysteine with six water molecules have been computed using the Time Dependent Density Functional Theory (TD DFT) [42] at B3LYP/6-311G\* level.

## 4. Results and Discussion-

### 4.1 Vibrational Frequencies

As mentioned earlier, the vibrational spectrum of the zwitterionic cysteine up to three water molecules does not give satisfactory results as the energy difference of 0.6 kcal/mole [31] between the zwitterionic and canonical form of cysteine is not sufficient for the stability of the zwitterionic cysteine in solution. This necessitates a reinvestigation of the vibrational spectrum of the zwitterionic cysteine with more explicit water molecules. The most stable structure of the zwitterionic cysteine with six water molecules is taken as starting geometry in our calculation. This complex is further optimized in the gas phase at B3LYP/6-311G\* level. Further, a single point energy calculation for this complex is performed using the gaseous optimized structure. Similar calculations have also been done for the most stable structure of canonical cysteine with six water molecules. It is found that zwitterionic cysteine is more stable by 4.2 kcal/mole (electronic energy) and 5.1 kcal/mole (free energy) than canonical cysteine if we consider six water molecules. The corresponding structures are given in Fig. 6. This indicates that six water molecules are sufficient to account the solvation at molecular level which was not truly defined in SCRF CPCM model in Gaussian. Thus, we expect that vibrational frequencies obtained at this level are more satisfactory rather than previous one. Our observed infrared and Raman frequencies are compared with the calculated frequencies in Table 1. A reasonable agreement is seen between the theoretical and the observed frequencies. The NH asymmetric stretch mode is computed for Z-cysteine (zwitterionic 3 cysteine) at  $3300\text{ cm}^{-1}$  but no such peak is seen in experimental measurements. The calculated intense band at  $3194\text{ cm}^{-1}$  is assigned as symmetric NH stretching vibration.

The corresponding vibration is also observed at 3157 and  $3175\text{ cm}^{-1}$  in the infrared spectra of the cysteine molecule taken in nujol mull and in solution respectively. Pawlukoje et al. [43] have also observed this peak at  $3190\text{ cm}^{-1}$  in their Raman spectrum. Thus our observed and calculated values are in reasonable agreement.

**Table 1. A comparison of the observed Infrared and Raman frequencies of the cysteine molecule with theoretically calculated frequencies of zwitterionic cysteine with six water molecules at B3LYP/6-311G\* level**

I. R. freq. (cm <sup>-1</sup> ) in mjol null	I.R. freq. in water (cm <sup>-1</sup> )	Raman freq. (cm <sup>-1</sup> )	Calculated I. R. freq. (cm <sup>-1</sup> )	Assignments
-----	-----	-----	3300(43)	Asym. NH <sub>2</sub> str.
3157	3175	-----	3194(535)	Sym. NH <sub>2</sub> str.
-----	2909	2921	2951(28)	CH str.
2870	-----	2892	2928(445)	NH str. hydrogen bonded with water
-----	2550	2519	2510(12)	SH str.
-----	2343	-----	-----	Combination bands
2083	2082	2071	-----	CH str. + other mode of vibration
-----	-----	1445	1444(72)	Asym. COO <sup>-</sup> str + NH <sub>2</sub> bend
1585	1415	-----	1581(22)	NH <sub>2</sub> wag.
1423	1424	1424	1440(7)	CH <sub>2</sub> sciss.
1394	1390	1398	1354(23)	CH bend + NH <sub>2</sub> bend + sym. COO <sup>-</sup> str.
1344	1345	1347	1313(213)	Sym. COO <sup>-</sup> str + NH <sub>2</sub> bend + CH bend
1294	1295	1295	1247(43)	CH <sub>2</sub> twist + NH <sub>2</sub> bend + CH bend
1195	1197	1201	1239(25)	CH <sub>2</sub> bend + SH bend
1140	1138	1142	1154(20)	CH <sub>2</sub> twist + NH <sub>2</sub> sciss + SH bend
1044	1042	1044	1039(72)	C-C str. + C-N str.
941	941	941	901(35)	C-COO <sup>-</sup> str. + C-N str. + C-SH def.
844	845	849	843(30)	SH bend + sym. COO <sup>-</sup> bend + CCH def.
821	820	821	774(120)	Inversion of C-C bend + sym. COO <sup>-</sup> bend
730	753	722	748(42)	Inversion of C-C + SH bend
692	691	693	642(35)	C-S str. + COO <sup>-</sup> bend
638	634	637	612(31)	C-C str. + COO <sup>-</sup> bend + CCH def.
534	538	540	504(4)	Inversion of C-N bend
500	-----	-----	474(12)	COO <sup>-</sup> bend + CCH bend
441	-----	448	437(8)	Inversion of C-C and C-N bend

Asym.: Asymmetric, Sym.: Symmetric, str.: Stretching, def.: Deformation, wag.: wagging, Sciss.: Scissoring, Values in bracket represent calculated intensity of infrared (IR) frequencies

**Table 2. Computed excitation states for the most stable zwitterionic cysteine with six water molecules and observed absorptions bands**

TD DFT calculations/B3LYP/6-311G* States	Oscillator strength(f)	Observed bands at different concentrations/different pH			
		0.005gm/ml	0.0025gm/ml	pH=2 at 0.005 gm/ml	pH=10 at 0.0025gm/ml
1	222.9(5.6); 0.0028	220	216	216	224
2	218.3(5.7); 0.0005	250	250	250	248
3	205.1(6.0); 0.0053				
4	195.3(6.3); 0.0057				
5	190.7(6.5); 0.0309				

**Table 3. A comparison between the optimized geometrical parameters for the most stable zwitterionic cysteine hydrated with six water molecules in gas phase at B3LYP/6-311G(d) level**

Bonds/bond angles	Zwitterionic cysteine-6H <sub>2</sub> O	Canonical cysteine-6H <sub>2</sub> O	Experimental values*
N-C <sub>α</sub>	1.49	1.46	1.49
C <sub>α</sub> -C	1.56	1.53	1.53
C-O	1.27	1.22	1.25
C <sub>α</sub> -C <sub>β</sub>	1.53	1.53	1.53
C <sub>β</sub> -S	1.84	1.84	1.84
C-C <sub>α</sub> -C <sub>β</sub>	111.7	113.2	111.6
C-C <sub>α</sub> -N	109.5	108.1	109.9
C <sub>β</sub> -C <sub>α</sub> -N	111.4	111.3	109.3
C <sub>α</sub> -C-O	117.1	121.9	118.1
C <sub>α</sub> -C <sub>β</sub> -S	114.3	113.4	114.4
O-C-O	128.2	124.1	125.7

Experimental values are taken from reference 45, Bond lengths are given in Å, bond angles in degrees



Similarly, the calculated frequency band at  $2928\text{ cm}^{-1}$  is assigned to NH stretching vibration which involves strong intermolecular hydrogen bonding with water. The corresponding peak is observed at  $2850$  and  $2892\text{ cm}^{-1}$  in the infrared and Raman spectra taken in solid form. The IR spectrum of cysteine in solution shows a peak at  $2989\text{ cm}^{-1}$ . In the Raman spectrum there appears a peak at  $2921\text{ cm}^{-1}$ . Both these bands belong to CH stretching mode. The calculated peaks match well to these. A broad peak is observed at  $2363\text{ cm}^{-1}$  but no such peak is seen in theoretically calculated spectrum. This may be attributed due to a combination of the bands at  $1295$  and  $1062\text{ cm}^{-1}$ . It may be assigned as a combination band of  $\text{CH}_2$  wagging and C-N stretching. The SH stretching vibration peak is observed at  $2550$  and  $2519\text{ cm}^{-1}$  in IR spectrum in aqueous solution and in Raman spectrum of solid sample respectively. Our calculated value corresponding to this peak is at  $2510\text{ cm}^{-1}$ . A peak observed at  $2071\text{ cm}^{-1}$  in the Raman, and at  $2083\text{ cm}^{-1}$  in IR (solid) and at  $2082\text{ cm}^{-1}$  in IR (aqueous solution) may be attributed to CN stretching vibration mixed with other modes because no such bands are found as the normal modes in their theoretically calculated frequencies. The peak observed in the Raman spectrum at  $1645\text{ cm}^{-1}$  is assigned as mixed vibrations of asymmetric  $\text{CO}_2$  and  $\text{NH}_3$  bending vibration. The corresponding theoretically calculated peak is at  $1664\text{ cm}^{-1}$ . Two other peaks observed in the IR spectra at  $1585$  and  $1615\text{ cm}^{-1}$  is assigned as the  $\text{NH}_3$  bending vibration. The corresponding theoretical peak is at  $1581\text{ cm}^{-1}$ . These assignments are very much similar to as reported earlier [44]. A band observed around  $1423\text{ cm}^{-1}$  in both IR and Raman spectra is assigned as the  $\text{CH}_2$  scissoring vibration [46]. Our calculated value for this band is  $1440\text{ cm}^{-1}$  which is in good agreement. Two frequencies observed around  $1390$  and  $1345\text{ cm}^{-1}$  in our experimental observations are assigned as the mixed vibrations of the symmetric  $\text{CO}_2$  stretching with  $\text{NH}_2$  bend and CH bend. Similarly, a peak at  $1060\text{ cm}^{-1}$  in our experimental observations is assigned as mixed vibrations of C-C and C-N stretching. As discussed above, the experimentally observed and our calculated vibrational frequencies for zwitterionic cysteine hydrated with six explicit water molecules are in better agreement. The other peaks observed in lower frequency sides also show a better agreement in the calculated and experimentally observed values (see Table 1).

#### 4.2 Electronic Absorption Spectra

The electronic spectrum of L- cysteine molecule has been recorded in the region of 200-400 nm using UV – Vis – NIR spectrophotometer. The investigations have been carried out at different concentrations and different pH value as shown in figure 5. For the concentration of 0.005 mg/ml, peaks appear at 220 nm and 250 nm. On reducing the concentration by one half, the first peak shifted to 216 nm while the peak at 250 nm remains unchanged. Similarly, at pH = 2, the peaks appeared at 216 nm, 250 nm while at pH=10, these peaks appear at 224 nm and 248nm. The vertical excitation energies obtained from TD DFT calculations of the most stable structure of zwitterionic cysteine with six water molecules has also been taken into considerations for comparison with above experimental observations. Following five singlet excited states are given in Table 2. Strong peak observed around 220 nm is well predicted by our TD DFT calculation.

#### 4.3 Geometry of zwitterionic Cysteine

Table 3 summarize the optimized bond lengths, bond angles for the most stable structure of cysteine (zwitterionic and canonical) hydrated with six water molecules at the 3LYP/6-311G(d) level. The geometrical parameters for zwitterionic cysteine are very close to those reported for a cysteine crystal by Gorbitz et al. [45]. This shows that the molecule in aqueous solution is in the zwitterionic form.

#### 5. Summary

FT-IR, Raman and Electronic absorption spectra of cysteine molecule are reported. Observed infrared and Raman spectra of the cysteine molecule are interpreted on the basis of the theoretically calculated infrared frequencies of zwitterionic cysteine with six water molecules. Fairly good agreement is found between the observed frequencies and the theoretically calculated frequencies. Two respective peaks at 220 nm and 250 nm are observed in the electronic absorption spectrum of the cysteine molecule.

The geometrical parameters of the most stable zwitterionic cysteine hydrated with six water molecules compare favorably with those for cysteine crystal.

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