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## On the spectroscopic analyses of aspartic acid

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### ABSTRACT

Aspartic acid was subjected to quantum mechanical calculations at B3LYP/3-21G\*\*. The amino acid was tested in gaseous phase then in the existence of two water molecules and when interacted with monovalent metal (Na) and then two units were made to interact with divalent metal (Cd). Vibrational frequencies bands were shifted into higher wavenumber as a result of hydration. The same was noticed also when Na interacted with aspartic acid through the hydrogen bonding of COOH group. The change in geometrical parameters was discussed in terms of changes in the COOH and NH<sub>2</sub> groups. The molecular point group was corresponding to C<sub>1</sub> point group for all the studied structures. The calculated total dipole moment increases as a result of complexation while slightly increased in case of hydration. Finally, the band gap energy decreases as a result of hydration and then further decreases as a result of complexation.

**Keywords:** Aspartic acid; FTIR; Vibrational spectrum; Molecular modeling; B3LYP/3-21G\*\*.

### INTRODUCTION

Amino acids are well known as the building blocks of proteins. Different spectroscopic analyses are directed toward amino acids for understanding both protein and enzyme behavior. Among the known natural amino acids, aspartic acid is found in three forms namely L-, D- and LD [1]. Aspartic acid has several advantages such as the determination of the age of living and nonliving systems [2-3]. It could be widely used in many areas of applications [4-5]. For industrial, medical and agricultural applications it is recommended to replace the conventional non-biodegradable polymers with biodegradable polymers such as Poly(aspartic acid) (PAA) [6]. Amino acids could be utilized as an effective tool for coordinating polymers and metal [7]. Application of amino acids as linkers has been utilized by several researchers [8-11]. More specific example could be given to aspartic acid which has now new role in some applications as a pH-responsive cyclopolymer containing residues of aspartic acid [12]. For the determination of heavy metals such as Hg(II) aspartic acid was coated with CdS/ZnS quantum dots in reverse micelles[13]. Molecular modeling at Hartree-Fock, MP2 and DFT were utilized to calculate and model the first stage of catalysis in the monomeric aspartic proteinases [14]. The level of theories was also utilized to study the anharmonic vibrational studies of L-aspartic acid [15]. DFT was utilized to calculate the different conformers of aspartic acid in both gas and liquid phases [16-18]. In the present work L-aspartic acid was studied using B3LYP/3-21G\*\* level of theory. First in gas phase then in the presence of three water molecules and then after interaction with Na and Cd the first through one aspartic unit while the second through two aspartic units.

### 2. CALCULATION DETAILS

Aspartic acid in gas phase was studied then the same molecule was studied in the presence of the three water molecules. Two complexes were tried the first one when Na interacted through the hydrogen bonding of COOH of aspartic acid. The second complex was tried when Cd interacted with two aspartic units through their hydrogen bonding.

All the studied structures were calculated with Gaussian09 program at Spectroscopy Department, National Research Centre, Egypt. Each structure was optimized using density functional theory at B3LYP [19-21] with 3-21G\*\* basis set. Vibrational spectrum was calculated for each structure at the same level of theory. The optimized structures are given in figure 1- a, b, c and d respectively.

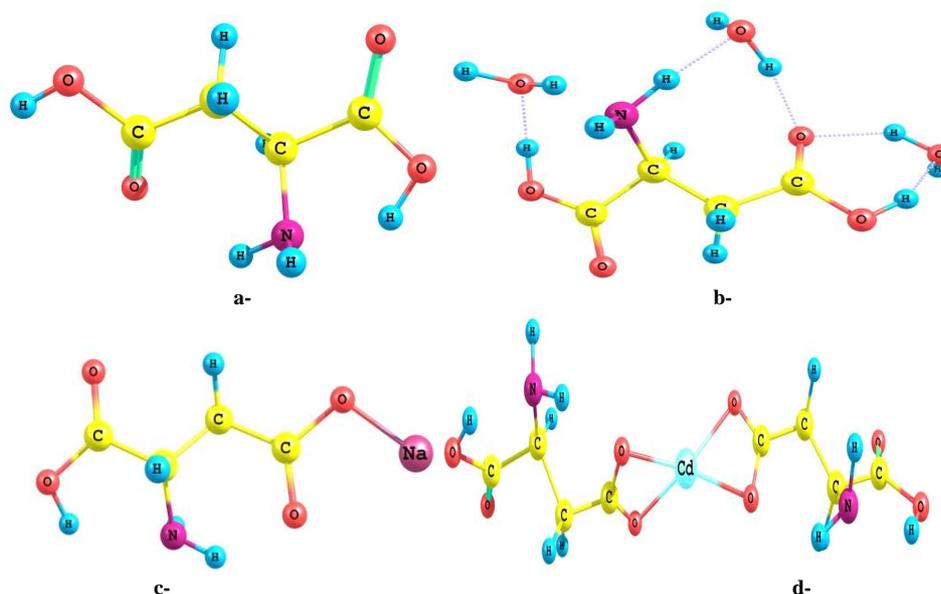


Figure1. B3LYP/3-21G\*\* optimized structure of a) aspartic acid, b) tri hydrated aspartic acid, c) aspartic acid interacted with Na through the hydrogen bonding of carboxyl group and d) two aspartic acid interacting with Cd through their carboxyl groups

## RESULTS AND DISCUSSION

The vibrational spectrum of aspartic acid are calculated at B3LYP/3-21G\*\* and the band positions and their assignments are presented in table 1. The table presents the characteristic bands for aspartic acid in gas phase, tri hydrated aspartic acid, aspartic Na complex and aspartic Cd complex. The assignment of the spectrum was aided by computer software, whereas, each band position is defined and the visualization of bands took place to make the assignment.

As indicated in the table a band of N-H symmetrical stretching vibration is located at  $3505\text{cm}^{-1}$ . The stretching band at  $1753\text{cm}^{-1}$  is assigned as C=O with a contribution of aspartic side chain. It is regarded that the N-H bends with C-N and C-C stretching give rise to a spectral band at  $1697\text{cm}^{-1}$ . C=O is a unique band in this structure as well as many other structures as described by Brian smith [22]. This band is very sensitive to the surrounding environment which in turn changes its vibrational characteristics. In case of free aspartic acid, the band could be as high as  $1780\text{cm}^{-1}$  [23]. A shift of about  $60\text{cm}^{-1}$  could be attributed to dimerization in solution phase [24-26], while weak hydrogen bonding makes it shifts about  $50\text{cm}^{-1}$  [39-40]. In the absence of specific interactions, the position of Amid I is correlated with Onsager's parameter,  $2(\epsilon - 1)/(2\epsilon + 1)$  [27-28], which reflects the intensity of local electrical fields stabilizing the Amid I electric dipole moment. This correlation is usually valid for Amid I around  $1730\text{cm}^{-1}$ , and could be used to monitor environmental changes of carboxylic amino acids inside proteins [28]. In molecular terms, this phenomenological correlation means that the Amid I is a function of the dielectric constant,  $\epsilon$ , of the environment. On the other hand, changing the dielectric constant shifts the equilibrium between the charged/deprotonated and neutral/protonated forms of Amid group, which is effectively the shift of the acid dissociation constant (pKa) [25]. Thus, for many practical cases ( $\nu\text{COOH} \sim 1730\text{cm}^{-1}$ ), the up shift in the position of the protonated carboxyl stretching frequency,  $\nu\text{COOH}$ , reflects an increase in the pKa of the COOH group ( $\sim 5\text{cm}^{-1}$  per pKa unit). That means that, the higher  $\nu\text{COOH}$  values corresponding to the elevated pKa, and the opposite correlation obtained for covalently bonded substituent at the alpha carbon atom makes it inapplicable in this case [26].

Table1. B3LYP/3-21G\*\*calculated vibrational spectra for aspartic acid, tri hydrated aspartic acid, aspartic Na complex and aspartic Cd complex

	Aspartic acid	Trihydrated aspartic acid	Aspartic Na complex	Aspartic Cd complex	Exp., [29]
N-H	3505	3518	3598	3472	3346
C=O	1753	1770	1499	1484	1731
N-H	1697	1719	1710	1710	1680

The effect of hydration upon aspartic acid was studied at the same level of theory; the calculated spectrum is indicated also in table 1. In the presence of three water molecules the vibrational characteristics are affected as in the following: The N-H symmetrical stretching vibration which was at  $3505\text{cm}^{-1}$  is shifted to  $3518\text{cm}^{-1}$ . The C=O stretching band at  $1753\text{cm}^{-1}$  is shifted to  $1770\text{cm}^{-1}$ . The last N-H bending band at  $1697\text{cm}^{-1}$  is shifted to  $1719\text{cm}^{-1}$ . It is clear that the hydration of aspartic acid has shifted its characteristic bands into higher wavenumbers. Another effect studied, when the hydrogen of the COOH is substituted with Na. The N-H symmetrical stretching vibration which was at  $3505\text{cm}^{-1}$  is shifted to  $3598\text{cm}^{-1}$ . The C=O stretching band at  $1753\text{cm}^{-1}$  is shifted to  $1499\text{cm}^{-1}$ . The last N-H bending band at  $1697\text{cm}^{-1}$  is shifted to  $1710\text{cm}^{-1}$ . It is clear that the interaction of aspartic with Na has shifted its characteristic bands to higher wavenumbers. Cadmium is complexed with two aspartic units as indicated in figure 1-d. The effect of complexation on the vibrational characteristics was as follows, the N-H symmetrical stretching vibration is further shifted toward lower wavenumber to be located at  $3472\text{cm}^{-1}$ . The same is noticed for the C=O band while the N-H bending is shifted to  $1710\text{cm}^{-1}$  similar to that for Na- complex.

Some calculated physical parameters are given in table 2. The molecular point group was corresponding to C1 point group for all the studied structures. The calculated total dipole moment was 4.903 Debye in gas phase. As a result of hydration the total dipole moment has slightly decreased to 4.647 Debye. Na has interacted with aspartic and enhances the total dipole moment to be 10.462 Debye. As far as divalent metal like cadmium interacts with two aspartic units the dipole moment for dimerization is supposed to be zero while the existence of cadmium increases the value of dipole moment to be 3.539 Debye. It is clear that complexation increases the total dipole moment while slight increase was recorded in case of hydration.

**Table 2. B3LYP/3-21G\*\*calculated point group, total dipole moment (TDM) as Debye, band gap energy ( $E_g$ ) as eV geometrical parameters of COOH including the bond angle C=O-C as ( $^\circ$ ), bond length LC=O as ( $\text{\AA}$ ) and LC-O as ( $\text{\AA}$ ), also the geometrical parameters of  $\text{NH}_2$  including the bond angle H-N-H as ( $^\circ$ ), bond length LN-H as ( $\text{\AA}$ ) for aspartic acid and tri hydrated aspartic acid**

	Aspartic acid	Tri hydrated aspartic acid	Aspartic Na complex	Aspartic Cd Complex	Exp., [15]
<b>Point group</b>	C1	C1	C1	C1	
<b>TDM</b>	4.903	4.647	10.462	3.539	
<b><math>E_g</math></b>	6.389	5.929	4.500	4.666	
<b>C=O-C (<math>^\circ</math>)</b>	122.9	122.1	123.1	118.9	124.1
<b>C=O (<math>\text{\AA}</math>)</b>	1.231	1.262	1.287	1.291	1.202
<b>C-O (<math>\text{\AA}</math>)</b>	1.374	1.338	1.306	1.308	1.306
<b>H-N-H (<math>^\circ</math>)</b>	108.23	110.45	107.67	108.78	114.9
<b>N-H (<math>\text{\AA}</math>)</b>	1.015	1.015	1.017	1.014	1.085
<b>N-H (<math>\text{\AA}</math>)</b>	1.016	1.035	1.018	1.019	1.010

The HOMO/LUMO band gap energy was also calculated as 6.389 eV and decreases as a result of hydration then further decreases as a result of complexation to be 5.929 eV, 4.500 eV and 4.666 eV respectively. The geometrical parameters are introduced for COOH and  $\text{NH}_2$  in terms of their bond lengths and bond angles. Regarding COOH the C=O-C angle was  $122.9^\circ$  then slightly decreased as a result of hydration ( $122.1^\circ$ ). Complexation is increasing the bond angle as for Na ( $123.1^\circ$ ) and decreasing it as for Cd ( $118.9^\circ$ ). The bond length C=O has increased from the gas phase to the complexation stage while the other bond length of COOH has decreased. As for the geometrical parameters of  $\text{NH}_2$ , the H-N-H angle has increased from gas phase into hydration ( $108.23^\circ$  to  $110.45^\circ$ ) then decreased as a result of Na complexation to be  $107.67^\circ$  then slightly increased due to Cd complex to be  $108.78^\circ$ . There are two NH bond lengths; both of them were nearly unchanged.

## CONCLUSION

Density functional theory at B3LYP/3-21G\*\* level was utilized for calculating the vibrational spectra, some physical as well as geometrical parameters for aspartic acid in gas phase. In addition the same level of theory also studied the same acid in the presence of three water molecules and in the presence of monovalent metal such as Na and divalent metal such as Cd. The changes in the geometrical parameters were noticed and recorded. The calculated results are in good agreement with experimental data. The agreement between experimental and calculated data indicates that this level of theory is quite adequate to study biophysical structures in different phases. In addition this level of theory required shorter computation time which could be achieved with personal computer.

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