VIBRATIONAL SPECTROSCOPIC STUDIES AND AB INITIO CALCULATIONS OF L-GLUTAMIC ACID 5-AMIDE

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ABSTRACT

The vibrational wavenumbers and corresponding vibrational assignments of L-Glutamic Acid 5-amide are examined theoretically using the Gaussian03 set of quantum chemistry codes. Comparison of the observed IR and Raman spectra with the calculated results by Hartree-Fock method is found in agreement with the experimental data. Theoretical infrared and Raman intensities are reported.
Keywords: *L-Glutamic acid, vibrational spectra, Hartee-Fock.*

INTRODUCTION

Amino acids, which constitute a very important class of biomolecules, can act as potential oxygen and nitrogen donor ligands. It has been found that they utilize their functional groups as fully as possible in metal conduction[1]. Copper (II) complexes of amino acids present important pharmacological interest as several of them show a wide spectrum of effects, including anti-inflammatory, antiulcer, anticonvulsant and even anti-tumoral activities[2-6]. The vibrational spectra of the copper (II) complexes of L-asparagine and L-glutamine are reported by Baran *et. al.*[7]. The vibrational and Raman spectrum of aspartic acid dipeptide and glutamic acid dipeptide were reported by Navarrete et. al.[8]. Ramirez and Navarrete[9] reported a normal coordinate calculation for the glutamic acid molecule by using the MNDO semi empirical method. In the present study, the FT-IR, FT-Raman and theoretical calculations of the wavenumbers for L-Glutamic acid 5-amide are reported.

EXPERIMENTAL

The FT-IR spectrum was recorded using a Perkin-Elmer FT-IR spectrometer. The spectral resolution was 4 cm . Standard KBr technique with 1 mg sample per 300 mg KBr was used. The FT-Raman spectrum was obtained on a Bruker IFS 66V NIR-FT instrument equipped with a FRA 106 Raman module. A Nd/YAG laser at 1064 nm with an output on 300 mW was used as the exciting source.

Computational Details:

Calculations of L-glutamic acid 5-amide are carried out with Gaussian03 program[10] using the Hartree-Fock/6-31G* basis set to predict the molecular structure and vibrational wavenumbers. Molecular geometry was fully optimized by Berny's optimization algorithm using redundant internal coordinates. Harmonic vibrational wavenumbers are calculated using the analytic second derivatives to confirm the convergence to minima on the potential surface. The wavenumber values computed at the HF level contain known systematic errors due to the negligence of electron correlation[11]. We therefore, have used the scaling factor value of 0.8929 for HF/6-31G* basis set. Parameters corresponding to optimized geometry of L-glutamic acid 5-amide (Fig.1) are given in Table 1. The absence of imaginary wave numbers on the calculated vibrational spectrum confirms that the structure deduced corresponds to minimum energy.

RESULTS AND DISCUSSION

The observed Raman and IR bands with their relative intensities, calculated values and assignments are given in Table 2.

-C(=O)NH$_2$ vibrations:

The NH$_2$ antisymmetric stretching vibrations[12] in the -C(=O)NH$_2$ group gives rise to a strong band in the region 3390 ± 60 cm^{-1} and the symmetric NH$_2$ stretch in the region 3210 ± 60 cm^{-1} with a somewhat weaker intensity. The HF calculations give these values at 3547 and 3428 cm^{-1} as υ_{as}NH$_2$ and υ_sNH$_2$. Baran *et al.*[7] reported the υ_{as}NH$_2$ at 3381, 3186 cm^{-1} and at 3398, 3203 cm^{-1} for copper complexes of L-asparagine and L-glutamine in the IR spectrum.

The C=O stretching vibration[12] in the associated state appears strongly at 1680 ± 40 cm^{-1}. The band at 1690 cm^{-1} in the IR spectrum, 1689 cm^{-1} in the Raman spectrum and 1761 cm^{-1} theoretically are assigned as υC=O. For the copper complexes of L-asparagine and L-glutamine υC=O is reported at 1637 (IR), 1620 (Raman) and 1620 (IR), 1602 cm^{-1} (Raman) respectively[7].

The NH$_2$ deformation band[12] δNH$_2$ is expected in the region 1610 ± 30 cm^{-1}. The highest values are furnished by F$_3$CC(=O)NH$_2$ and MeC(=O)NHC(=O)NH$_2$ (1640 cm^{-1}) and the lowest by KOC(=O)C(=O)NH$_2$, NaOC(=O)C(=O)NH$_2$ (1584 cm^{-1}). Most primary amides[12] display this δNH$_2$ band at 1610 ± 20 cm^{-1}. For the title compound this δNH$_2$ band is observed at 1640 cm^{-1} in IR, 1645 cm^{-1} in Raman spectrum. The ab initio calculation give this mode at 1639 cm^{-1}. δNH$_2$ amide is reported at 1680 (IR), 1694 (Raman) and 1664 (IR), 1695 cm^{-1} (Raman) for metal complexes of L-asparagine and L-glutamine[7].

The C-N stretching vibration of the amide group is only weakly to moderately active in the region 1385 ± 85 cm^{-1} and is difficult to detect. Formamide gives this band at 1309 cm^{-1}, acetamide at 1398 cm^{-1}, propanamide and butanamide at about 1420 cm^{-1} [12]. The υC-N amide stretching band is reported at 1363 (IR), 1351 cm^{-1} (Raman) for copper complexes of L-asparagine and at 1402 (IR), 1398 cm^{-1} (Raman) for copper complexes of L-glutamine[7]. For the title compound the band at 1420 cm^{-1} in the IR and 1411 cm^{-1} in the Raman spectrum are assigned as υC-N amide band. The HF calculation gives a value 1403 cm^{-1}.

The in-plane NH$_2$ rock absorbs weakly to moderately in the region 1125 ± 45 cm^{-1}. In the spectrum of formamide[12] this vibration is assigned at 1090 cm in the liquid state and 1150 cm^{-1} in the vapour state. The band at 1136 cm^{-1} in IR, 1133 cm^{-1} in Raman are assigned as NH$_2$ rocking mode for the title compound. The ab initio calculations give the mode at 1134 cm^{-1}. The amide band, absorbing in the region 775 ± 45 cm^{-1}, is assigned to the NH$_2$ out-of-plane twist and is also under the influence of the C=O out-of-plane deformation[12]. The wagging mode ωNH$_2$ is expected in the region 670 ± 60 cm^{-1} is a mixed vibration with a contribution from the C=O out-of-plane deformation. The NH$_2$ wag is usually clearly separated from the twist and is easy to recognize by its broad band structure. The out-of-plane twist τNH$_2$ is observed at 808 cm^{-1} in the IR spectrum and 823 cm^{-1} theoretically. The wagging mode ωNH$_2$ is observed at 675 cm^{-1} in IR, 645 cm^{-1} in Raman spectrum and at 690 cm^{-1} (HF). The wagging ωNH$_2$ amide is reported at 669 (IR), 663 (Raman) and 665(IR) and 661 cm^{-1} (Raman)[7].

Primary amides give the C=O in-plane deformation in the region 610 ± 70 cm^{-1} with a weak to moderate intensity[12]. For most of the –C(=O)NH$_2$ compounds, the δC=O is situated at the lower wavenumber side of the ωNH$_2$ band[12]. The weak to medium and sometimes broadish band in the region 560 ± 70 cm^{-1} is assigned to the C=O out-of-plane deformation with a contribution from the NH$_2$ wagg[12]. For the title compound, δC=O is observed at 600 cm^{-1} in IR, 611 cm (Raman) , 601 (HF) and γC=O at 542 (IR), 546 (Raman) and at 553 cm^{-1} theoretically. The in-plane skeletal

deformation is a mixed vibration described as the external –C-N deformation or ρ–C(=O)-N, comparable with the –C(=O)-O rocking vibration in carboxylic acids or esters[12]. The band at ~ 458 cm^{-1} in both spectra is assigned as δC-N deformation for the title compound. The HF calculation gives the mode at 435 cm^{-1}. The –C(=O)NH$_2$ torsion[12] is expected in the region 150 $\pm$ 50 cm^{-1}. The band at 122 cm^{-1} in the IR spectrum and at 114 cm^{-1} (HF) is assigned as the torsional mode of C(=O) NH$_2$.

Amino group vibrations:
In associated aliphatic and alicylcic primary amines, the NH$_2$ antisymmetric stretching vibration occurs[13] at 3365 $\pm$ 25 cm^{-1}. 1-Butanamine absorbs at 3370 cm^{-1}, F$_3$CCH$_2$NH$_2$ takes the high wavenumber side with 3385 cm^{-1} and in amines with broadly on the α-carbon atom this band tends to shift to lower wavenumbers[12]. In dilute solution or in the vapour state, the υ_{as}NH$_2$ appears[12] at 3420 $\pm$ 40 cm^{-1}. Aliphatic and alicyclic primary amines in the associated state display υ_sNH$_2$ in the region 3290 $\pm$ 30 cm^{-1} , and at 3350 $\pm$ 40 cm^{-1} in a gas or in dilute solution. In the vibrational spectra of copper complexes of L-asparagine and L-glutamine the υ_{as}NH$_2$ amino is reported at 3265 , 3296, 3278 cm^{-1} in the IR spectrum[7]. The υ_sNH$_2$ is reported at 3249, 3234 (Raman) and 3232 cm^{-1} in the IR spectrum [7]. For the title compound we have observed υ_{as}NH$_2$ amino at 3400 cm^{-1} in both spectra and at 3427 cm^{-1} theoretically. The υ_sNH$_2$ is observed at 3343 cm^{-1} (IR), 3200 (Raman) and at 3340 cm^{-1} theoretically.
The NH$_2$ scissoring vibration[12] gives rise to a broad strong band in the region 1600 $\pm$ 50 cm^{-1}. The band observed at 1590 cm^{-1} (IR), 1600 cm^{-1} (Raman) and 1607 cm^{-1} (HF) is assigned as δNH$_2$ for the title compound. For copper complexes of L-glutamine[7] this band is reported at 1574 and 1586 cm^{-1} .
According to Roeges[12] the rocking/twisting NH$_2$ mode is expected in the region 1160 $\pm$ 140 cm^{-1}. In methanamine the NH$_2$ twist (1195 cm^{-1}) is coupled to the methyl rock. In aliphatic amines this mode is mixed with the methylene twist and also with the C-N stretching vibration. The band at 1200 cm^{-1} in both spectra and at 1203 cm^{-1} (HF) is assigned as ρ/τ NH$_2$ for the title compound.
Associated α-saturated primary amines show a characteristic very broad diffuse ωNH$_2$ band between 1000 and 700 cm^{-1}, with a maximum absorption at 840 $\pm$ 55 cm^{-1}. For copper complexes of L-asparagine and L-glutamine the wagging NH$_2$ is reported at 804, 780 cm and 783, 777 cm^{-1} respectively[7]. For the title compound, the band observed at 775 cm^{-1} (IR), 778 cm^{-1} (Raman) and 748 cm^{-1} (HF) is assigned as ωNH$_2$ mode. The NH$_2$ torsion is expected in the region 290$\pm$130 cm^{-1} and in α-saturated amines the region is reduced to 280 $\pm$ 70 cm^{-1} [14,15].
Medium to weak absorption bands for the unconjugated C-N linkage in primary, secondary and tertiary aliphatic amines[16] appear in the region of 1250 – 1020 cm^{-1}. The vibrations responsible for these bands involve C-N stretching coupled with the stretching of adjacent bonds in the molecule. Baran *et al.*[7] reported a value at around 1129 cm^{-1} as C-N amine stretching frequency. For the title compound the band at 1109 cm^{-1} in the IR spectrum, 1100 cm^{-1} in the Raman spectrum and 1097 cm^{-1} (HF) is assigned as υC-N mode.

COOH group vibrations:
The –C(=O)OH group is best characterized by the OH stretch, the C=O stretch and the OH out-of-plane deformation and even by the C-O stretch and the OH in-plane deformation. The C=O stretching vibration in the spectra of carboxylic acids gives rise to strong band in the region 1725 $\pm$ 65 cm^{-1} . In the vapour state the monomer absorbs at a wavenumber 50 cm^{-1} higher[12]. In the present case no bands are experimentally observed. The HF calculation give the mode at 1832

cm^{-1} as υC=O carboxyl. The OH in-plane deformation, coupled to the C-O stretching vibration, is expected in the region 1390 ± 55 cm^{-1}. The C(=O)-O stretching vibration, coupled to the OH in-plane deformation, exhibits a moderate to strong band in the region 1250 ± 80 cm^{-1}. The out-of-plane OH deformation[17] exhibits a moderate band in the region 905 ±65 cm^{-1}. The C=O in-plane deformation is weakly to moderately active in the region 725 ± 95 cm^{-1} .Most carboxylic acids display γC=O in the region 595 ± 85 cm^{-1} which is in the vicinity of that of methyl and ethyl esters. -C(=O)O deformation or rock has a weak to moderate intensity and appears in the region 445 ± 120 cm^{-1}. For glutamic acid dipeptides and aspartic acid dipeptide, the γOH is reported[8] at ~ 940 cm^{-1}. The bands observed at 925 cm^{-1} (IR), 930 cm^{-1}(Raman) and 945 cm^{-1} (HF) are assigned as γOH of carboxylic group. The deformation C=O bands are calculated to be at 736 and 532 cm^{-1}.

CH$_2$ group vibrations:
The vibrations of the CH$_2$ group, the asymmetric stretch υ_{as}CH$_2$, symmetric stretch υ_sCH$_2$, scissoring vibrations δCH$_2$ and wagging vibration ωCH$_2$ appear in the regions 3000 ± 50, 2965 ± 30, 1455 ± 55 and 1350 ± 85 cm , respectively[12,18]. Absorption arising from C-H stretching in alkenes occurs in the general region[16] of 3000 – 2840 cm^{-1}. The positions of the C-H stretching vibrations are among the most stable in the spectrum. For the two CH$_2$ groups, the asymmetric CH$_2$ stretching bands are observed at 2971, 2929 cm^{-1} in the IR spectrum and at 2967, 2933 cm^{-1} in the Raman spectrum. The theoretically calculated values are 2950 and 2901 cm^{-1}. The symmetrical CH$_2$ group stretching bands are observed at 2889 cm^{-1} in the Raman spectrum and 2857 cm^{-1} in the IR spectrum while the HF calculations give these modes at 2897 and 2867 cm^{-1}. The CH stretching vibration is not observed experimentally. The HF calculations give a value at 2871 cm^{-1}. For copper complexes of L-asparagine and L-glutamine the CH$_2$ stretching vibrations are reported at 2927, 2948, 2926 and 2945, 2923, 2931, 2916 cm^{-1} respectively[7]. For the CH stretching Baran *et. al.*[7] observed a very weak band at 2870 and 2887 cm^{-1}.
The in-plane deformation of CH$_2$ bands are observed at 1490, 1460 cm^{-1} in the IR spectrum and at 1500, 1456 cm^{-1} in the Raman spectrum. The calculated values are 1470 and 1456 cm^{-1}. The wagging modes of ωCH$_2$ group are observed at 1360, 1340 cm^{-1} (IR) and 1356, 1322 cm^{-1} (Raman) and at 1371, 1351 cm^{-1} theoretically for the title compound. The twisting mode τCH$_2$ group are observed at 1280, 1260 cm^{-1} (IR) and at 1278, 1256 cm^{-1} (Raman) and at 1299, 1276 cm^{-1} theoretically. Baran *et. al.*[7] reported 1460, 1440, 1332, 1308, 1299, 1250, 1232 and 1225 cm^{-1} as these modes. The rocking modes[12] ρCH$_2$ is expected in the range 895 ± 85 cm^{-1}. The band at 856 cm^{-1} in the Raman spectrum, 850, 721 cm^{-1} in the IR spectrum and 854, 729 cm^{-1} (HF) are assigned as ρCH$_2$ modes for the title compound. The torsional modes are seen in the low wavenumber range[12].

Other vibrations:
Baran *et. al.*[7] reported the CC stretching bands in the range 870 – 1117 cm^{-1} and CC bending modes below 400 cm^{-1}. For glutamic acid dipeptide the υCC modes[8] in the range 910 – 1090 cm^{-1}. For glutamic acid in the non-zwitterionic form[19] υCC is in the range 1094 – 846 cm and δCCC is at 386, 337 and 211 cm^{-1}. In the present case the bands at 1082, 1055, 1000, 900 cm^{-1} (IR) and 1056, 1000, 900 cm^{-1} (Raman) and 1068, 1038, 999, 899 cm^{-1} (HF) are assigned as the stretching CC modes. The bending modes δCCC are calculated to be at 399, 347, 272, 231, 211 cm^{-1} and observed at 339, 296, 222, 198 cm^{-1} in the Raman spectrum.

Concerning the bond distances the carbon-carbon and carbon-hydrogen bond lengths are close to the experimental values reported for glycine and alanine amino acids in the gaseous state[20,21] namely 1.081Å (C-H), 1.526 Å (C-C) and 1.071 Å(C-H), 1.522 Å (C-C) respectively. With regard to the carbon-carbon distances, the HF results are sensitive to the influence of the oxygen atom O_{18}, thus decreasing the C_{13}– C_{14} length with respect to the central C-C bonds. Concerning the bond angles, the optimized values of NH_2 and COOH moieties compare well with previous results reported for other amino acids. As an example, the bond angles of the NH_2 and COOH moieties are near to the data reported for the alanine molecule from ab initio calculations[22] namely 126.1° (O-C-O), 111.8° (O-C-C), 122.1° (O=C-C) and 111.5° (C-O-H) for the carboxylic group and 113.6° (C-C-N), 112.9° (mean for the two C-N-H) and 110.5° (H-N-H) for the amino group. The ab initio data values (Table 1), for the carboxylic acid, C_5–O_8 = 1.3183 Å, C_5=O_9 =1.1855 Å, O_8–H_{10} = 0.9562 Å are closer to the theoretical results obtained for the serine molecule[23], namely 1.203 Å (C=O), 1.361 Å (C-O), 0.965 (O-H) and for glutamic acid[19] namely 1.2074 Å (C=O), 1.3487 Å (C-O), 0.9533 Å (O-H).

Fig-1 Optimized geometry of L-Glutamic Acid 5-amide
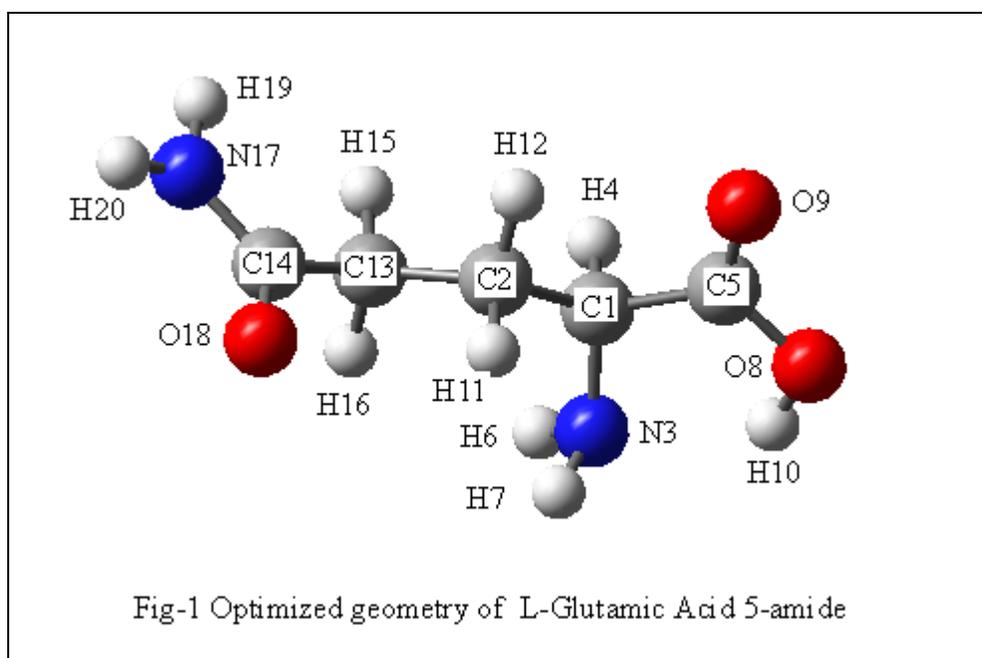
Table-1: Optimized geometrical parameters of the title compound, atom labeling is according to Fig.1

Bond Lengths (Å)				
C_1–C_2 1.5316	C_1–N_3 1.4599	C_1–H_4 1.0871	C_1–C_5 1.5360	C_2–H_{11} 1.0846
C_2–H_{12} 1.0820	C_2–C_{13} 1.5309	N_3–H_6 0.9996	N_3–H_7 1.0028	C_5–O_8 1.3183
C_5–O_9 1.1855	O_8–H_{10} 0.9562	C_{13}–C_{14} 1.5194	C_{13}–H_{15} 1.0863	C_{13}–H_{16} 1.0861
C_{14}–N_{17} 1.3523	C_{14}–O_{18} 1.1992	N_{17}–H_{19} 0.9924	N_{17}–H_{20} 0.9956	

Bond angles (˙)

A(2,1,3) 115.1 A(2,1,4) 109.2 A(2,1,5) 110.7 A(3,1,4) 107.1 A(3,1,5) 109.8
A(4,1,5) 104.2 A(1,2,11) 109.4 A(1,2,12) 108.6 A(1,2,13) 112.7 A(11,2,12) 106.9
A(11,2,13)109.0 A(12,2,13) 110.0 A(1,3,6) 112.4 A(1,3,7) 111.6 A(6,3,7) 107.7
A(1,5,8) 115.1 A(1,5,9) 122.4 A(8,5,9) 122.5 A(5,8,10) 108.4 A(2,13,14) 111.3
A(2,13,15) 110.4 A(2,13,16) 110.5 A(14,13,15) 111.4 A(14,13,16) 105.8
A(15,13,16) 107.2 A(13,14,17) 116.2 A(13,14,18) 121.4 A(17,14,18) 122.4
A(14,17,19) 122.4 A(14,17,20) 117.9 A(19,17,20) 118.2

Dihedral angles(˙)

D(3,1,2,11) 53.5 D(3.1.2,12) 169.9 D(3,1,2,13) -68.0 D(4,1,2,11) 174.0
D(4,1,2,12) -69.6 D(4,1,2,13) 52.6 D(5,1,2,11) -71.8 D(5,1,2,12) 44.6
D(5,1,2,13) 166.7 D(2,1,3,6) 87.6 D(2,1,3,7) -33.5 D(4,1,3,6) -34.1
D(4,1,3,7) -155.2 D(5,1,3,6) -146.7 D(5,1,3,7) 92.2 D(2,1,5,8) 144.4
D(2,1,5,9) -38.1 D(3,1,5,8) 16.2 D(3,1,5,9) -166.3 D(4,1,5,8) -98.3
D(4,1,5,9) 79.3 D(1,2,13,14) 169.8 D(1,2,13,15) -65.9 D(1,2,13,16) 52.5
D(11,2,13,14) 48.1 D(11,2,13,15) 172.4 D(11,2,13,16) -69.2 D(12,2,13,14) -68.8
D(12,2,13,15) 55.5 D(12,2,13,16) 173.9 D(1,5,8,10) -3.7 D(9,5,8,10) 178.8
D(2,13,14,17) 129.0 D(2,13,14,18) -52.7 D(15,13,14,17) 5.3 D(15,13,14,18) -176.4
D(16,13,14,17)-110.9 D(16,13,14,18) 67.4 D(13,14,17,19) -10.3 D(13,14,17,20) -176.4
D(18,14,17,19) 171.5 D(18,14,17,20) 5.4

Table-2: Infrared, Raman spectral data and calculated wavenumbers and band assignments for L-Glutamic Acid 5-amide

HF(cm^{-1})	IR intensities (KM/Mole)	Raman activity ($Å^4$/AMU)	IR (cm^{-1})	Raman (cm^{-1})	Assignments
3547	55.06	46.69			$\upsilon_{as}NH_2$ amide
3533	211.03	29.58			υOH
3428	63.47	98.56			υ_sNH_2 amide
3427	11.72	52.59	3400 m	3400 w	$\upsilon_{as}NH_2$ amino
3340	6.46	63.29	3343 w	3200 w	υ_sNH_2 amino
2950	14.98	25.47	2971 s	2967 m	$\upsilon_{as}CH_2$
2901	27.88	54.42	2929 s	2933 s	$\upsilon_{as}CH_2$
2897	8.93	33.58		2889 w	υ_sCH_2
2871	22.05	112.96			υCH
2867	14.72	34.39	2857 s		υ_sCH_2
1832	358.20	5.86			$\upsilon C=O$ carboxyl
1761	398.14	6.18	1690 m	1689 w	$\upsilon C=O$ amide
1639	43.34	4.93	1640 s	1645 w	δNH_2 amide
1607	131.66	3.16	1590 m	1600 m	δNH_2 amino
1470	7.78	1.66	1490 s	1500 m	δCH_2
1456	9.46	14.48	1460 m	1456 s	δCH_2
1403	150.95	1.50	1420 m	1411 s	$\upsilon C-N$ amide
1397	290.56	0.99	1380 w		δOH
1371	56.59	7.25	1360 w	1356 m	ωCH_2
1351	298.02	0.71	1340 s	1322 s	ωCH_2

1299	2.09	11.88	1280 m	1278 m	τCH_2
1276	38.68	0.74	1260 w	1256 w	τCH_2
1237	11.46	1.07			$\upsilon C(=O)O$
1218	26.92	5.46			δCH
1203	12.32	2.14	1200 w	1200 w	$\rho/\tau NH_2$ amino
1134	8.42	3.34	1136 w	1133 m	ρNH_2 amide
1097	7.77	5.72	1109 w	1100 s	$\upsilon C-N$ amino
1068	23.78	0.94	1082 w		$\upsilon C-C$
1038	15.05	7.94	1055 w	1056 m	$\upsilon C-C$
999	19.06	3.92	1000 w	1000 m	$\upsilon C-C$
945	57.33	2.29	925 w	930 m	γOH
899	58.68	10.63	900 w	900 s	$\upsilon C-C$
854	105.67	0.60	850 w	856 s	ρCH_2
823	4.25	1.49	808 w	800 w	ρNH_2 amide
748	5.01	2.54	775 w	778 m	ωNH_2 amino
736	44.41	0.96			$\delta C=O$
729	120.49	1.65	721 w		ρCH_2
690	8.80	3.28	675 w	645 m	ωNH_2 amide
601	34.95	0.32	600 w	611 s	$\delta C=O$ amide
553	6.30	2.69	542 w	546 m	$\gamma C=O$ amide
532	22.60	2.06			$\gamma C=O$
507	15.14	3.86		480 w	$\rho C(=O)O$
435	1.01	0.26	458 w	459 s	$\delta C=N$ amide
399	5.71	0.52			δCCC
347	13.91	0.82		339 m	δCCC
272	21.45	1.27		296 m	δCCC
263	19.50	0.47			t NH_2 amino
231	17.68	1.84		222 s	δCCC
211	275.52	0.61		198 s	δCCC
114	0.86	0.55		122 s	t $C(=O)NH_2$
94	2.72	0.29			tCC
62	5.79	0.28			tCC
41	5.41	0.72			tCOOH
21	11.52	2.02			tCC

υ - stretching; ω - wagging; δ - in-plane deformation; γ - out-of-plane deformation; ρ - rocking; τ - twisting; t - torsional; m – medium; w – weak; s- strong; subscript : as – asymmetric; s - symmetric.

REFERENCES
1. B.Y.K.Ho, J.A.Zubieta, J.J.Zuckerman, *J. Chem. Soc. Chem. Commun*. **2**, 88 (1975)
2. J.R.J.Sorenson, *J. Med. Chem*. **19**, 135 (1976).
3. J.R.J.Sorenson in : H.Sigel (Ed.) *Metal Ions in Biological systems,* 14, Marcel Dekker, New York (1982).
4. E.J.Baran, *Acta Farm. Bonaerense*. **4**, 125 (1985).

5. N.Farrell, *Transition Metal Complexes as Drugs and Chemotherapeutic Agents*, Kluwer, Dordrechi (1989).
6. E.J.Baran, *Mini Rev. Med. Chem.* **4**, 1 (2004).
7. E.J.Baran, I.Viera, M.H.Torre, *Spectrochim. Acta.* **66A**, 114 (2007)
8. J.T.L.Navarrete, V.Hernandez, F.J.Ramirez, *J. Mol. Struct.* **348**, 249 (1995).
9. F.J.Ramirez, J.T.L.Navarrete, *Spectrochim. Acta* **51A**, 293 (1995).
10. M.J.Frisch, G.W.Trucks, H.B.Schlegel, G.E.Scuseria, M.A.Robb, .R.Cheeseman, J.A.Montgomery Jr., T.Vreven, K.N.Kudin, J.C.Burant, J.M.Millam, .S.Iyengar, J.Tomasi, V.Barone, B.Mennucci, M.Cossi,G.Scalmani, N.Rega, G.A.Petersson, H.Nakatsuji, M.Hada, M.Ehara, K.Toyota,R.Fukuda, J.Hasegawa, M.Ishida, T.Nakajima, Y.Honda, O.Kitao,H Nakai, M.Klene, X.Li, J.E.Knox, H.P.Hratchian, J.B.Cross,C. Adamo, J. Jaramillo, R.Gomperts, R. E.Stratmann, O.Yazyev, A.J.Austin, R.Cammi, C.Pomelli, J.W.Ochterski, P.Y.Ayala, K.Morokuma, G.A.Voth, P.Salvador, J. J.Dannenberg,V.G.Zakrzewski, S. Dapprich, A.D.Daniels, M.C.Strain,O.Farkas, D.K.Malick, A.D.Rabuck, K. Raghavachari, J. B. Foresman, J.V.Ortiz, Q.Cui, A.G.Baboul, S.Clifford,J. Cioslowski, B.B.Stefanov, G.Liu, A.Liashenko, P.Piskorz, I.Komaromi, R.L. Martin, D.J.Fox, T.Keith, M.A.Al-Laham,C.Y.Peng, A. Nanayakkara, M.Challacombe, P.M.W.Gill, B.Johnson, W.Chen, M.W.Wong, C.Gonzalez, and J. A. Pople, *Gaussian03*, Revision C.02, Gaussian, Inc., Wallingford CT (2004).
11. J.B.Foresman, E.Frisch in: *Exploring Chemistry with Electronic Structure Methods: A Guide to Using Gaussian*, Gaussian Pittsburg, PA (1996).
12. N.P.G.Roeges, *A Guide to the Complete Interpretation of Infrared Spectra of Organic Structures*, Wiley, New York (1994).
13. L.Segal, F.V.Eggerton, *Appl. Spectrosc.* **15**, 112 (1961).
14. S.M.Craven, F.F.Bentley, *Appl. Spectrosc.* **26**, 449 (1972).
15. S.M.Craven, F.F.Bentley, D.F.Pensenstadler, *Appl. Spectrosc.* **26**, 647 (1972).
16. R.M.Silverstein, F.X.Webster, *Spectrometric Identification of Organic Compounds, sixth ed.*, Wiley, Asia (2003).
17. I.Fischmeister, *Spectrochim. Acta* **20**, 1071 (1964).
18. N.B.Colthup, L.H.Daly, S.E.Wiberly, *Introduction to Infrared and Raman Spectroscopy*, second ed. Academic Press, New York (1985).
19. J.T.L.Navarrete, L.Bencivenni, F.Ramondo, V.Hernandez, F.J.Ramirez, *J. Mol. Struct.(Theochem).* **330**, 261 (1995).
20. K.Iijima, K.Tanaka, S.Onuma, *J. Mol. Struct.* **246**, 257 (1991).
21. K.Iijima, B.Beagley, *J. Mol. Struct.* **248**, 133 (1991).
22. K.Siam, V.J.Klimkowski, J.D.Ewbank, C.V.Alsenoy, L.Schafter, *J. Mol. Struct. (Theochem)* **110**, 171 (1984).
23. C.Van Alsenoy, S.Kulp, K.Siam, V.J.Klimkowski, J.D.Ewbank, L.Schafer, *J. Mol. Struct. (Theochem)* **181**, 169 (1988).