Polish J. of Environ. Stud. Vol. 15 No. 4A (2006), 91-93

The Hydration Effect on the Structure and Spectroscopic Characteristics of Magnesium Glutamate – Glycine

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Abstract

The hydration effect on the structural and spectroscopic characteristics of magnesium glutamate-glycine [Mg(glu-gly)] has been examined using density functional theory (DFT) calculations at the B3PW91 level.

Keywords: magnesium glutamate, amino acid, DFT calculations, infrared spectrum

Introduction

Magnesium salts of the glutamic acid modified by such amino acids as glycine and arginine are widely used in the pharmaco-therapy due to their key role in the transport processes of magnesium. The hydration of magnesium salts improves their solubility that facilitates the release process into the surrounding [1]. Recently, structural and spectroscopic investigations by DFT method of [Mg(glu-gly)] and [Mg(glu-arg)] isolated molecules have been reported [2]. The aim of our present report is to examine the hydration effect on the structure and vibrational frequencies of [Mg(glu-gly)].

Theoretical and experimental methods

The optimized geometry and vibrational frequencies for [Mg(glu-gly)] · 4 H_2O have been calculated, similarly as for the isolated molecule [2], by the DFT method at the B3PW91 level with the 6-31+G* basis set. The atomic partial charges were calculated using the natural population analysis. All computations were performed with the GAUSSIAN 03 program package [3].

Infrared spectra of [Mg(glu-gly)] · 4 H_2O have been recorded in the range of 4000 - 400 cm^{-1} on a Bio-Rad FTIR6000 spectrometer at room temperature using the KBr pellet technique.

Results and discussion

The obtained optimized [Mg(glu-gly)] · 4 H_2O complex with the atom numbering used during calculations is shown in Fig. 1a (atoms in the water molecules are not numbered). In Table 1 selected molecular properties and vibrational frequencies of [Mg(glu-gly)] · 4 H_2O and isolated molecule are compared. Because of the limited scope of the present report the comparison concerns only the most characteristic vibrations and these properties which differ noticeably.

Comparison of bond lengths for [Mg(glu-gly)] · 4 H_2O and [Mg(glu-gly)] shows the greatest differences for Mg-O2 and Mg-O3 distances which are longer by 0.1912 and 0.1809 Å, respectively, for the hydrated form. Moreover, noticeable differences are observed for C1-O1, C5-O4, C1-O2 and C5-O5. In the first two cases interatomic distances are longer in the hydrated complex by 0.0312 and 0.0 330 Å, respectively, whereas in the two remaining cases they are shorter to the same degree. The angle differences between [Mg(glu-gly)] · 4 H_2O and [Mg(glu-gly)] are clear in the neighbourhood of the Mg atom only and the greatest change concerns the O2-Mg-O3 angle which is smaller in

the hydrated form by 62.5° in comparison with that in the isolated molecule. Comparison of the partial atomic charges in [Mg(glu-gly)] · 4 H_2O and [Mg(glu-gly)] indicates that we have to be concerned with the greatest differences regarding the Mg atom and oxygen atoms in the glutamate part. In the case of [Mg(glu-gly)] the natural population analysis method places negative charges at O1, O2, O3 and O4 atoms (-0.604, -1.015, -1.010 and -0.590, respectively) and a positive charge at Mg atom (1.819). In the case of [Mg(glu-gly)] · 4 H_2O, O1 and O4 increase their negative charges to -0.677 and -0.711, respectively, whereas O2 and O3 decrease their negative charges to -0.935 and -0.937, respectively; Mg decreases its positive charge to 1.753.

From the theoretical energy values of [Mg(glu-gly)] · 4 H_2O, [Mg(glu-gly)] and H_2O the binding energy of the studied complex has been calculated and its value is 106.2 kcal/mol.

In Table 1 the calculated frequencies of characteristic C=O stretching vibrations and two characteristic modes involving the Mg atom markedly are listed. We see that the calculated non-scaled frequencies of C=O stretching vibrations for [Mg(glu-gly)] · 4 H_2O are shifted towards lower frequencies in comparison with those of [Mg(glu-gly)]. When the scaling procedure is taken into account, the scaled frequencies reproduce the corresponding experimental frequencies slightly better than in the case of the isolated molecule (the common scaling factor for [Mg(glu-gly)] · 4 H_2O, taken from the calibration of the corresponding theoretical DFT results with the most intense experimental bands, has been estimated as 0.930). The 165.9 and 177.4 cm^{-1} frequencies of [Mg(glu-gly)] · 4 H_2O, attributed to the τ(OMgO) and δ(OMgO) modes [1], respectively, are shifted towards higher frequencies but, unfortunately, these modes occur in the far-infrared and are relatively weak. In Fig. 1b, the predicted scaled vibration frequencies for [Mg(glu-gly)] · 4 H_2O are compared with the experimental spectrum and a sufficient agreement between theory and experiment is observed. This agreement indicating the presence of hydrate complexes in the investigated sample is better than that obtained in the case of the isolated molecule.

Table 1. Comparison of selected geometry parameters, partial atomic charges and fundamental frequencies of [Mg(glu-gly)] · 4 H_2O and [Mg(glu-gly)].

Molecular property	**[Mg(glu-gly)] · 4 H_2O**	**[Mg(glu-gly)]**
Bond [Å]		
C1-O1	1.2463	1.2151
C1-O2	1.2868	1.3216
C5-O4	1.2448	1.2118
C5-O3	1.2967	1.3326
Mg-O2	2.0430	1.8518
Mg-O3	2.0433	1.8624
Angle [°]		
C1-O2-Mg	117.63	121.91
C5-O3-Mg	117.34	112.91
O2-Mg-O3	92.00	154.52
Atomic charge		
O1	-0.677	-0.604
O2	-0.935	-1.015
O3	-0.937	-1.010
O4	-0.711	-0.590
Mg	1.753	1.819

Vibrational frequencies [cm^{-1}]					
Experimental	Calculated non-scaled	Calculated scaled	Calculated non-scaled	Calculated scaled	Assignment [1]
1639.0	1756.3	1633.4	1813.6	1650.4	ν(C5=O)
1598.3	1699.2	1580.3	1794.2	1632.7	ν (C1=O)
1567.0	1661.6	1545.3	1760.3	1601.9	ν (C6=O)
--	177.4	165.0	151.0	137.4	τ(OMgO)
--	165.9	154.3	138.2	125.8	δ(OMgO)

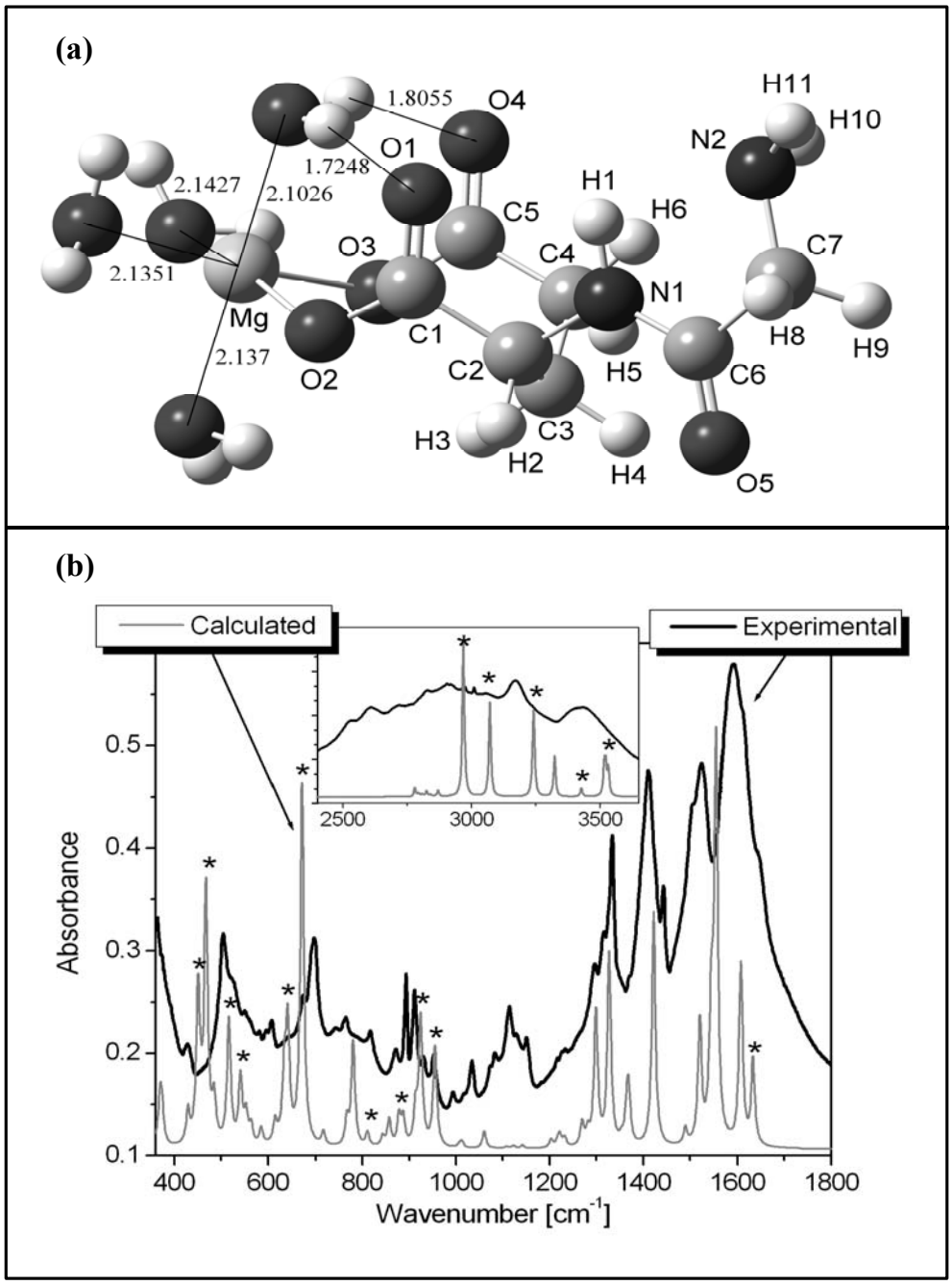

Fig. 1. (a) Optimized structure of [Mg(glu-gly)] · 4 H_2O, (b) Comparison of B3PW91 calculated infrared spectrum of [Mg(glu-gly)] · 4 H_2O with experiment (* denotes water vibrations)

References

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