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Hydration of L-tyrosine in Aqueous Solution. An FT-IR and Raman Spectroscopic and Theoretical Study

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INTRODUCTION

QM/MM calculations have been carried out in order to study the theoretical structures of L-tyrosine as well in gas phase as in aqueous solution. The molecule was characterized by infrared and Raman spectroscopies in solid phase and aqueous solution (Figure 1).

Optimized geometries for different specie derived from L-tyrosine have been calculated taking into account the solvent effects by using the SCRF theory with the GAUSSIAN program.¹ The theoretical structures in gas phase were simulated by using AMBER² force field while in aqueous solution were performed with the PCM model³ and then, the results were analyzed and compared.

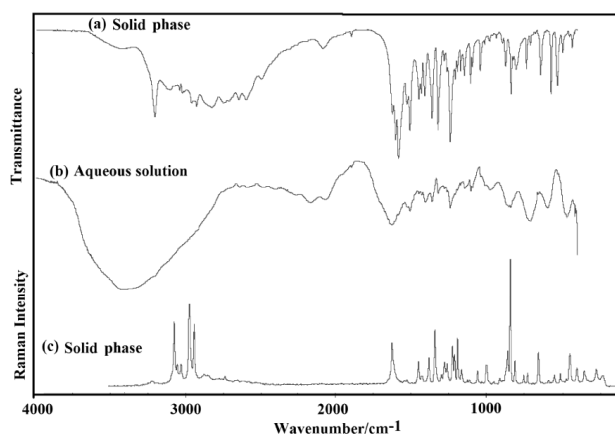


FIGURE 1. Experimental spectra of the L-tyrosine compound: a) Infrared spectrum in solid phase, b) Infrared spectrum in aqueous solution and, c) Raman spectrum in solid phase.

Results and Conclusions

Three different stable conformations with geometry C_1 were obtained according to the position of the $H_2N-C-COOH$ or $^+H_3N-C-COO^-$ moieties with respect to the

benzyl ring, named C_I, C_{II} and C_{III} conformers. Calculations by using both basis sets predict for the C_I conformer a lower energy value and, for this, is the most stable conformer. The higher dipole moments values are obtained for all zwitterions, as is expected because are specie highly hydrated in aqueous solution. The calculated solvation energies by means of the PCM model for the zwitterions specie with the two basis sets shows a significant decreasing from C_{III} to C_I. The smaller solvation energies values are obtained for the C_I specie whiles the higher values for the C_{III} specie because are zwitterions charged with a higher dipole moments. The molecular volume for all species by using both QM/MM methods shows that the zwitterions are hydrated in aqueous solution because the volumes notably increase, in relation to the values in gas phase. Significant effects on the geometrical and vibrational frequencies are found for those studied L-tyrosine specie.

Afterwards, a complete assignment of all observed bands in the IR and Raman spectra in solid state and in aqueous solution for neutral and zwitterions species were performed by using DFT/B3LYP calculations combined with Pulay's SQMFF methodology.⁴ Moreover, DFT, Natural Bond Orbital (NBO)⁵ and topological properties, by means of atoms and molecules theory AIM⁶ calculations were obtained to analyze the energies and geometrical parameters of its three conformers in gas phase as well as the magnitude of the intramolecular interactions.

Good agreement between theoretical and available experimental results of dipole moment values in aqueous solution⁷ and harmonic vibration frequencies were found.

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REFERENCES

1. Program Gaussian 03, GAUSSIAN, Inc. Pittsburgh, PAA, USA, 2003.
2. W. D. Cornell, P. Cieplak, C. I. Bayly, I. R. Gould, K. M. Merz Jr., D. M. Ferguson, D. C. Spellmeyer, T. Fox, J. W. Caldwell, P. A. Kollman, *J. Am. Chem. Soc.* **117**, 5179-5197, (1995).
3. Miertus, S.; Scrocco, E.; Tomasi, J. *Chem. Phys.* **55**, 1117-1129, (1998).
4. Pulay, P.; Fogarasi, G.; Pongor, G.; Boggs J. E.; Vargha, A. *J. Am. Chem. Soc.*, **105**, 7037-7047, (1983).
5. Reed, A. E.; Weinhold, F. *J. Chem. Phys.* **83**, 1736-1740, (1985).
6. F. Biegler-Köning, J. Schönbohm, D. Bayles, AIM2000; A Program to Analyze and Visualize Atoms in Molecules, *J. Comput. Chem.*, **22**, 545-559, (2001).
7. S. A. Brandán, M. Córdoba, M. A. Acuña-Molina, *An. Asoc. Quím. Arg.* **79(5)**, 189-196 (1991).