

# DFT and Spectroscopic Study of Chelation of Kaempferol with Iron

Marković Z.,<sup>(1)</sup> Dimitrić-Marković J.<sup>(2)</sup>, Marković S.<sup>(3)</sup>

<sup>(1)</sup> Department of Biochemical and Medical Sciences, University of Novi Pazar, Vuka Karadžića bb, Novi Pazar 36300, Serbia: zmarkovic@np.ac.rs

<sup>(2)</sup> Faculty of Physical Chemistry University of Belgrade Studentski trg 12-16, Belgrade 11000, Serbia: markovich@ffh.bg.ac.rs

<sup>(3)</sup> Faculty of Science, University of Kragujevac, 12 Radoja Domanovića, Kragujevac 34000, Serbia: mark@kg.ac.rs

Spectroscopic studies indicate kaempferol as a ligand capable of chelating iron (II) only in a narrow range of pH values. On addition of iron (II) to alkaline buffered solutions of kaempferol long-wavelength band shifts bathochromically ( $\Delta\lambda \approx 30$  nm) giving simultaneous rise to the new absorption band which corresponds to the complex formed. The structure and corresponding UV spectrum of the complex kaempferol iron 1:1 were investigated using the B3LYP/6-31G\*\* method.

The iron coordination occurs with the loss of the hydroxyl group protons, and leads to the formation of 2 planar 1:1 complexes, where the iron (II) ion is ligated with molecule of kaempferol via O4 and O5 (4-5 complex), and via O3 and O4 (3-4 complex). It was found that 4-5 complex is by 1.58 kcal mol<sup>-1</sup> more stable than 3-4 form. The results for the 4-5 complex are here presented.

The agreement between the observed and predicted wavelengths and intensities of the complex absorption bands is satisfactory. The maximum of the complex band, whose experimental value is 402 nm, is predicted at 416.0 nm. This is essentially a HOMO-1→LUMO transition (32%), accompanied with HOMO→LUMO transition (38%). This peak is assigned as mostly metal-to-ligand charge transfer (MLCT). The shapes of the orbitals included in the transition (Fig. 1), confirm that the transition is associated with significant charge-transfer from the metal to the ligand moieties.

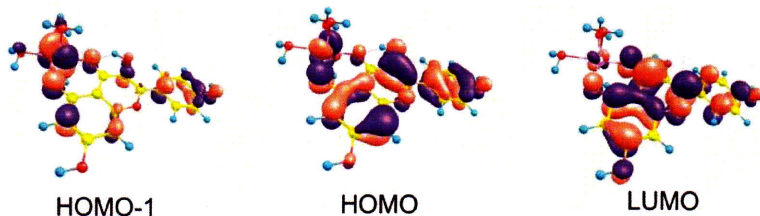


Fig. 1 The occupied and virtual orbitals responsible for the UV spectrum of the 4-5 complex

## References:

- [1] Ren, J.; Meng, S.; Lekka, Ch. E.; Kaxiras, E. *J. Phys. Chem. B* **2008**, *112*, 1845-1850.

## Insights into the mechanism of Hydroxypropylphosphonic acid epoxide

Milaczewski

<sup>(1)</sup> Jerzy Haber Institute of Catalysis and Surface Chemistry, ul. Niezapomnianej 8, 01-224 Warszawa, Poland

The final step in the biosynthesis of hydroxypropylphosphonic acid epoxide by crystallographic studies, the substrate iron in a bidentate fashion, which activates electron donors activated iron center in subsequent step, abstraction of hydroxyl intermediate that produces fosfomycin.

Concerning the mechanism of the substrate activation and cyclization, responsible for hydrogen atom abstraction mechanism, we have undertaken quantum barriers to consecutive steps of the catalytic reaction mechanism for the second product is 2-oxopropylphosphonic acid. Some light on the stereospecificity and chemical model of the active site including and additionally residues from the iron center computed at the B3LYP/LACV3P\*\*//6-311++(2d,2p) as well as dispersion interactions and ZPE corrections.

## References:

- [1] Higgins, L. J.; Yan F.; Liu P.; Liu H.; Drösgemüeller, G. *J. Am. Chem. Soc.* **2004**, *126*, 1481-1490.  
[2] Yan F.; Moon S.; Liu. P.; Zhao Z.; Lipscomb, W. D. *J. Am. Chem. Soc.* **2005**, *127*, 1481-1490.  
[3] Mirica L. M.; McCusker K. P.; Munos L. *J. Am. Chem. Soc.* **2006**, *128*, 8123.